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THE REARRANGEMENT AND SUBSTITUTION OF SOME TRIPHENYLMETHYL
ARYLSULFINATES

BY

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A THESIS

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ABSTRACT

The half life for the first order rearrangement of triphenylmethyl-2-methylbenzenesulfinate to triphenylmethyl-2-methylbenzene sulfone in chloroform at room temperature, has been found to be twenty minutes. The 4-methyl analogue rearranges at twice this rate, while the 2,6-dimethyl analogue does not undergo rearrangement, even under more vigorous reaction conditions.

These rearrangements have been found to proceed by an ionization mechanism, rather than an internal, cyclic, non-ionizing rearrangement.

In concurrent rearrangement and substitution, the presence of a common capturable ion pair intermediate has been detected. No specification can be made as to whether this ion pair is of the intimate or solvent-separated type, but the presence of dissociated ions is precluded by conduction of the experiments in chloroform.

In high dielectric constant solvents, rearrangement and substitution products have been found partly to result from a common ion pair intermediate, but mainly, from different ionic species.

The reactions of trityl perchlorate with various tetra-n-butylammonium salts have been used as models, and have been of assistance in the interpretation of the results.

CHAPTER I

The first part of the book is devoted to a general introduction to the subject of the history of the human mind. It is divided into three main sections: the first section deals with the history of the human mind in general, the second section deals with the history of the human mind in particular, and the third section deals with the history of the human mind in the future.

The second part of the book is devoted to a detailed examination of the history of the human mind in the past. It is divided into two main sections: the first section deals with the history of the human mind in the ancient world, and the second section deals with the history of the human mind in the modern world.

The third part of the book is devoted to a detailed examination of the history of the human mind in the future. It is divided into two main sections: the first section deals with the history of the human mind in the near future, and the second section deals with the history of the human mind in the distant future.

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INTRODUCTION

The physical and chemical properties of triarylcarbonium ions have been of long-standing interest to organic chemists, and therefore, derivatives of these systems have been widely and intensely investigated. At the turn of the century, conductivity studies of triphenylmethyl (trityl) chloride in liquid sulfur dioxide by Walden (1) and Gomberg (2), served to establish the ready ability of these species to ionize, which characteristic is due to the exceptional stability associated with the triphenylcarbonium ion. Later conductivity work established the effect of changes in structure on the ionization (3,4,5), the determination of entropies and enthalpies (6), and the effect by substituents on the stabilization of these cationic species (6,7,8).

Conductivity has its limitations in that it does not give a measure of the concentration of ion pairs and molecules in the conducting medium, but only determines the amount of free ions present. Later workers have overcome this difficulty by the use of other methods :

(a) Spectrophotometry, which measures both the free ions and ion pairs present, and from which data the relative concentrations of each contribution is determinable (9), is applicable to the trityl system because of the intense yellowish-red colouration characteristic of the ion.

(b) Chemical detection - by the trapping of carbonium ions with various nucleophiles, in conjunction with salt effects and kinetic studies, estimates of the types of species present may be made, and thus, the reaction mechanism elucidated. Within

the past sixteen years, most of the work on trityl systems has been conducted with trityl chloride, and both of these methods have been exhaustively used for determinations of equilibria constants and reaction processes.

Much controversy has been associated with these investigations. In 1951, Evans reported the values of the equilibria constants K_1 and K_2 for the ionization of trityl chloride to ion pairs and free ions in nitromethane (10). In determining the extinction coefficient for the trityl cation in this solvent, he observed that the absorbance values changed with time. However, this change was slow enough to allow fairly accurate measurements to be made. This work was repeated by Leffler (11). He found that the results of Evans could not be reproduced, despite precautions which were taken against the use of impure reagents. Evans in 1957 (12), reported the reproducibility of his results. Recently, Smith acknowledges the accuracy and reproducibility of Evans' work (13). From vapour-phase chromatography studies, it was apparent that the discrepancy lay in the nitromethane, which Smith found to be impure. When pure solvent was used, $K_{eq.}$ for trityl chloride was found to be 3.48×10^{-4} , which value agreed within 10% of that reported by Evans and Pocker (14). It would appear therefore, that a high degree of error is introduced in the results from these systems unless meticulous care is exercised in experimental technique and purification of reagents.

The other important controversial phase of investigation of trityl systems has involved the mechanism of the solvolysis of trityl chloride in solvents of low dielectric constants. Some

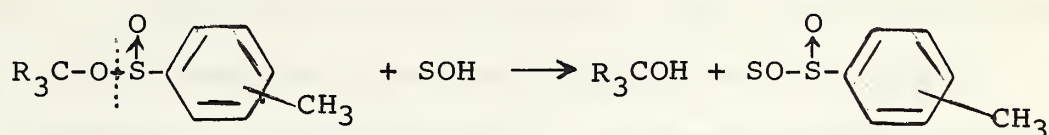
investigators have considered solvent molecules in their role as both electrophiles and nucleophiles in rate-determining and pre rate-determining processes, and the mechanism of nucleophilic substitution has been thoroughly considered (15-23). Other workers have expressed various opinions as to the interpretations of these results (24-26). At the present time, it would appear that both schools of thought agree that in the substitution and solvolysis of trityl chloride, attack by the nucleophile occurs on the carbonium ion of an ion pair intermediate.

A critical analysis of these data has been summarized by Winstein (27): "For a first venture into benzene as solvent, trityl chloride is an unfortunate choice of substrate system. On the practical side, there are great experimental difficulties, and at least part of the experimental procedure of Ingold and co-workers is unsound, as already pointed out by Swain. On the theoretical side, trityl chloride is a poor choice of substrate. This is because it does not afford any direct estimate of K_1 the ionization rate constant, and therefore, no indication of the real magnitude of ion pair return accompanying methanolysis or exchange."

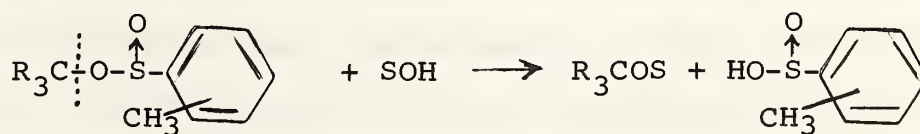
The nature of the rearrangement of sulfinate esters to sulfones has been of interest to a number of earlier workers. Arcus, Balfe and Kenyon studied the conversion of α -methylbenzyl 4-methylbenzenesulfinate into α -methylbenzyl 4-methylphenyl sulfone (28), and concluded that the mechanism of rearrangement of the ester occurred partly by an intramolecular process, and partly by ionization. Later, Cope, Morrison and Field (29) effected



the rearrangement of allyl benzenesulfinate and related compounds, without reaching a final decision on the mechanism. Recently, however, MacFayden and Stevens (30) have shown carbonium ions to be intermediates in the rearrangement of some diaryl methyl arene-sulfonates to sulfones in acetic acid, and have also observed the inability of the methyl, phenyl, benzyl, and o-nitrobenzyl derivatives of 4-methylbenzenesulfinate to rearrange to their sulfones under a variety of conditions. To recent workers, the most common facet of interest in sulfinate systems has been an elucidation of the type of bond cleavage which occurs during the solvolysis of these esters. The type of cleavage occurring in a particular system on solvolysis can readily be determined by an examination of the reaction products. Either carbon-oxygen or sulfur-oxygen bond cleavage can take place on alcoholysis. If sulfur-oxygen bond cleavage occurs, then parent carbinol and a new benzenesulfinate result as products.



However, if carbon-oxygen bond fission occurs, benzenesulfinic acid and an alkyl ether are produced.



Exclusive sulfur-oxygen bond cleavage has been observed by Bunton and Hendy (31, 32) in the hydrolysis of methyl and benzhydryl 4-methylbenzenesulfonates in H_2O^{18} enriched, 60% by volume dioxane-water, using sodium hydroxide as base. No O^{18}

was observed to be incorporated in the alcoholic product, and no carbon-oxygen bond cleavage occurred. The acid-catalyzed hydrolysis gave carbon-oxygen bond fission products.

Herbrandson and Cusano (33) have observed sulfur-oxygen bond cleavage in the ethanolysis of (-)-menthyl (+)-p-iodobenzene-sulfinate to yield the ethyl ester as product.

None of the work previously mentioned has been concerned with an elucidation of the mechanistic details associated with the rearrangement of the sulfinate esters to the sulfones. MacFayden and Stevens (30) found carbonium ions as intermediates in these rearrangements, but have not considered the mechanism to occur fractionally by intramolecular and ionization processes. Nor has any information been produced, or proposals offered by these authors to explain the nature of the ionic species which might have been generated in the rearrangement. Recently Darwish and McLaren (34) have examined the mechanism of the rearrangement of a number of arenesulfinates bearing the above mentioned factors in mind, and this work has also been examined on this basis.

Originally, triphenylmethyl 2,6-dimethylbenzenesulfinate was selected as substrate for these investigations for a number of reasons. The original idea in mind was to investigate the concurrent solvolysis and rearrangement of this ester with the intention of elucidating the detailed reaction mechanism, that is, to determine the types of ionic species which might exist as intermediates in such processes. To allow for this, it was necessary to prevent nucleophilic substitution at sulfur, and thus enable carbon-oxygen bond cleavage to take place to generate ion

The first part of the paper is devoted to a general discussion of the problem of the existence of solutions of the system of equations (1) for arbitrary values of the parameters α and β . It is shown that the system (1) has solutions for arbitrary values of the parameters α and β if and only if the condition $\alpha + \beta = 1$ is satisfied. In this case the solutions are unique and can be found by the method of successive approximations.

In the second part of the paper the problem of the stability of the solutions of the system (1) is considered. It is shown that the solutions of the system (1) are stable with respect to the initial conditions if and only if the condition $\alpha + \beta = 1$ is satisfied. In this case the solutions are stable with respect to the initial conditions and the method of successive approximations can be used to find them.

In the third part of the paper the problem of the asymptotic behavior of the solutions of the system (1) is considered. It is shown that the solutions of the system (1) tend to zero as $t \rightarrow \infty$ if and only if the condition $\alpha + \beta = 1$ is satisfied. In this case the solutions tend to zero as $t \rightarrow \infty$ and the method of successive approximations can be used to find them.

In the fourth part of the paper the problem of the periodicity of the solutions of the system (1) is considered. It is shown that the solutions of the system (1) are periodic if and only if the condition $\alpha + \beta = 1$ is satisfied. In this case the solutions are periodic and the method of successive approximations can be used to find them.

pairs, which it was hoped would yield both the sulfone (by rearrangement) and solvolysis products (from substitution by solvent molecules). In order to accomplish this, the 2,6-dimethylphenyl group was selected so that the methyl groups might effectively shield the lone pair of electrons on sulfur. When it was later realised that solvolysis rates of trityl 2,6-dimethylbenzenesulfinate were immeasurably fast, even in absolute ethanol, and that the compound did not rearrange to give sulfone, our interest was directed to rearrangement and substitution studies of the less hindered trityl analogues, the O-methyl and p-methylbenzenesulfates, and to substitution studies of the 2,6-dimethyl ester. In so doing, it was hoped that an elucidation of the rearrangement mechanism might be possible, that is, whether it was an internal, cyclic, non-ionizing process, or an ionization process, which might be operative. Also, it was believed that a determination of the types of intermediates in these processes might be allowed from these studies. Furthermore, both the practical and theoretical difficulties associated with trityl chloride (27) might well be overcome, and thus, some information could be contributed to the existing data on trityl systems.

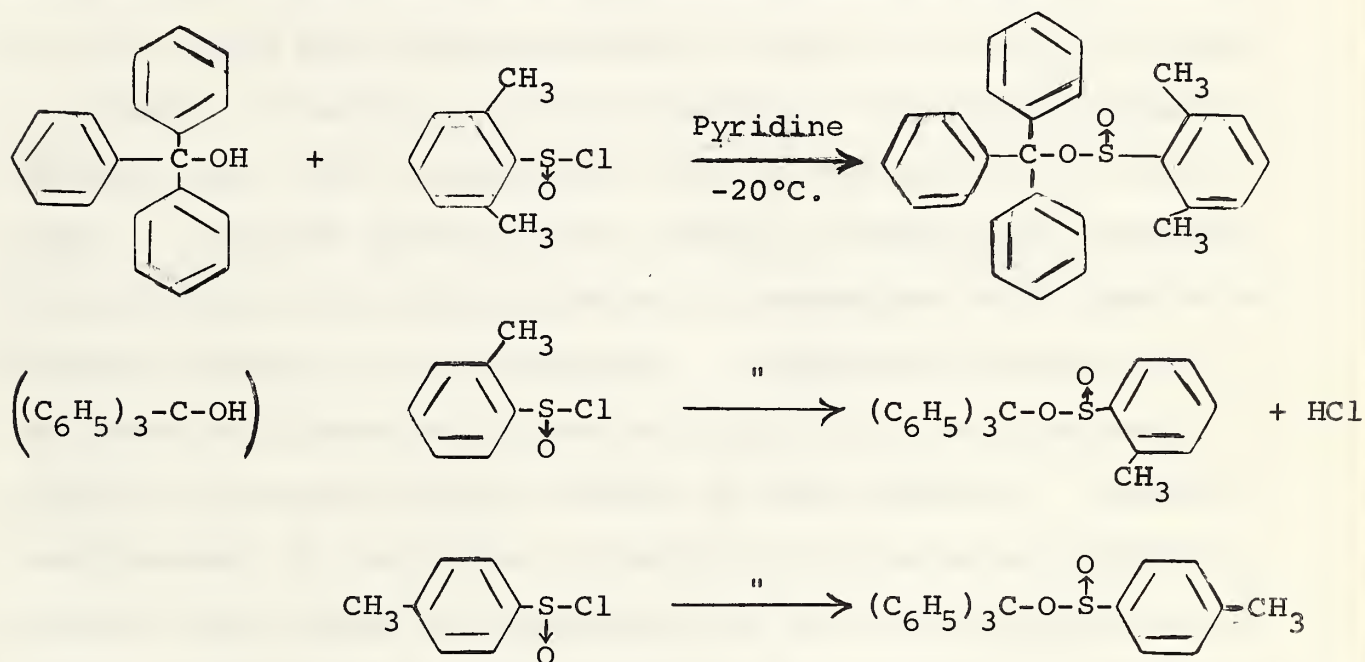
CHAPTER 1.

Preliminary Investigations of the Reactivity of Triphenylmethyl-sulfinates and sulfones.

Some Solvolytic Reactions of Triphenylmethylsulfinates and Sulfones

RESULTS

The synthesis of these esters was accomplished by the reaction of triphenylcarbinol with the appropriate sulfinyl chloride, in pyridine as solvent, at -15 to -20°C. In order to ensure complete utilization of the triphenylcarbinol, a mole ratio of one to two in alcohol to acid chloride was maintained:



The crucial step in this preparation was the work-up procedure. If the pyridine was completely removed by neutralization with hydrochloric acid, then hydrolysis of the esters readily occurred on washing the ethereal extracts with water. When all of the pyridine was not removed, the compounds could be isolated in good yields. In order to verify the necessity of pyridine in the prevention of hydrolysis of these esters in the work-up

procedure, and in order to determine what solvolyzing agent was effective in bringing about the hydrolysis, the following series of experiments were conducted. Individual solutions of trityl 2,6-dimethylbenzenesulfinate in a number of common solvents of low dielectric constant (chloroform, benzene, pentane and ether) were separately washed with water and water solutions of sodium carbonate or hydrochloric acid as outlined in Table I. The ester could be recovered only when an excess of pyridine was present. In the other cases, complete hydrolysis of the ester was found to occur, and the only product isolated after removal of the solvent was triphenylcarbinol, except in the case of ether as solvent. The other hydrolysis product, 2,6-dimethylbenzene sulfinic acid, was not recovered since it was lost to the water layer. Infrared spectra of the reaction products gave positive identification of triphenylcarbinol by comparison with spectra of authentic samples of this compound. Comparison of spectra of the reaction product with those of trityl 2,6-dimethylbenzenesulfinate revealed definite absence of this compound. Further establishment of the degree of purity of the isolated triphenylcarbinol was allowed by a comparison of the melting points of the isolated product with that of pure triphenylcarbinol. With ether as solvent, apparently all of the 2,6-dimethylbenzenesulfinic acid was not removed in the extraction procedure, hence the reported yields of triphenylcarbinol in excess of 100%, and the low melting point of the isolated product relative to that of pure triphenylcarbinol. 2,6-Dimethylbenzenesulfinic acid was identified here as a reaction product from infrared spectra.

Once the esters were isolated using this procedure, they

Table I

Hydrolysis of solutions of Trityl 2,6-dimethylbenzenesulfinate at 25°C.

Solvent	Ester (M.)	Water	Hydrochloric acid	Sodium carbonate	Pyridine	Triphenylcarbinol % Yield	2,6-dimethyl ester % Yield
Chloroform	0.064	+				88.5	-
Benzene	0.014	+				86.5	-
Pentane	0.014	+	+	+		55.5	151-156
	0.006	+	+			42.4	150-155
	0.005	+		+		58.8	151-156
	0.005	+				70.0	150.155
Ether	0.028	+				143 ^a	96-99
	0.029	+		+		130 ^a	87-89
	0.029	+	+	+		144 ^a	86-87
	0.030	+	+	+	+	-	100

^a Crude product contains 2,6-dimethylbenzenesulfonic acid in addition to triphenylcarbinol.

were recrystallized from ether, and their identity and purity established by analysis of infrared and N.M.R. spectra. Complementing this, product analyses of reaction products, (by titrimetry and chromatography), from solvolyses in ethanol revealed an 88-95% purity for these compounds.

The solvolysis of trityl 2,6-dimethylbenzenesulfinate by absolute ethanol at room temperature was found to be a very rapid process. The allowed reaction time was two hours, approximately thirty minutes of which was required for dissolution of the ester. The reaction products were isolated by extraction with ether-water mixtures to ensure complete removal of the ethanol, (the sulfinic acid being removed by this procedure), and were then chromatographed on neutral alumina. The products isolated in this manner included trityl ethyl ether, benzophenone, and triphenylcarbinol (see Table II). In the presence of the base 2,6-lutidine which was added to prevent acid catalysis from occurring, trityl ethyl ether was isolated as the only reaction product (Table II). An interpretation of these results will be presented in the discussion.

Solvolysis of the ester when conducted in ethanol-water mixtures, yielded 2,6-dimethylbenzenesulfinic acid and trityl ethyl ether as products (Table II). The percentage yield of acid was determined by titrimetry, while that of the trityl ethyl ether was effected by extraction of the titrated mixture with ether, followed by elution chromatography, and identification of the product by its infrared spectrum.

When the solvolysis was conducted in dioxane-water mixtures, the reaction rate appeared to be somewhat slower than that in ethanol-water (Table II).

Table II

The solvolysis of some trityl arenesulfonates and sulfones at 25°C.

Solvent	Trityl benzene- sulfonate	(M.)	2,6- lutidine (M.)	Trityl ethyl ether	Products 2,6-dimethyl acid	(% Yield) ^c Benzo- phenone	Triphenyl- carbinol	Time (hr.)
Ethanol	2,6-dimethyl	0.0250	-	27.2		22.1	43.0	2
	2,6-dimethyl	0.0250	0.0304	88.5		-	-	2
	2-methyl	0.0248	0.0320	88.0		-	-	2
	2-methyl sulfone	0.0194	0.0322	88.6		-	-	1
Ethanol- water	2,6-dimethyl	0.0243	-	68.0 ^b	94.6 ^a	-	-	0.16
Dioxane- water	2,6-dimethyl	0.0255	-		86.0 ^a	-	-	1

^a Determined by titrimetry

^b Determined by chromatography of titrated mixture

^c % Yield is based on starting ester, but uncorrected for purity of ester which is 88-95% pure; products isolated by chromatography.

The yield of products reported in Table II are uncorrected for the purity of the starting esters, which, however, are 88-95% pure.

A comparison of the reactivity of the 2,6-dimethyl ester with ethanol in chloroform, in the presence, or absence, of 2,6-lutidine, was also obtained. In the absence of 2,6-lutidine, very rapid ethanolysis occurs, the solution changes from colourless to yellow, and 2,6-dimethylbenzenesulfinic acid precipitates from solution as white amorphous crystals. Trityl ethyl ether is the other reaction product. When the base is present, no visible reaction is discernible, and the 2,6-dimethyl ester was recovered unchanged from the reaction mixture. The results are given in Table III.

Table III

Ethanolysis of trityl 2,6-dimethylbenzenesulfinate in chloroform
at 25°C.

Ester (M)	Ethanol (M)	2,6-lutidine (M)	Products	Observed reaction time (min.)
0.0250	0.0490	0.0313	ester	150
0.0266	\div 0.2460 ^a	-	ether + acid	very rapid
0.0258	\div 0.2460 ^a	0.4100	ester	30

^a Analytical Reagent grade chloroform used.

The monosubstituted ester, trityl 2-methylbenzenesulfinate, reacts in an analogous manner to the 2,6-dimethyl ester in solvolysis. In absolute ethanol, complete solvolysis occurred at room temperature within an hour, forty minutes of which was required for dissolution of the compound. The isomer of the 2-methyl ester, trityl 2-methyl-

phenyl sulfone, was also found to undergo very rapid ethanolysis. (see Table II). No sulfone was isolated as a product from the ethanolysis of either the 2-methyl or 2,6-dimethyl esters. Since these reactions appeared to be so rapid in absolute ethanol, no comparison of the relative rates of solvolysis of these compounds was possible in this solvent.

Steric inhibition to the Rearrangement of Trityl 2,6-dimethyl-benzenesulfinat.

A variety of methods were used in an attempt to synthesise trityl 2,6-dimethylphenyl sulfone. Oxidations of trityl 2,6-dimethylphenyl sulfide in acetic acid with potassium permanganate, as suggested by Vogel for the preparation of sulfones (35), yielded starting sulfide as the product. A hydrogen peroxide oxidation of the sulfide in acetic acid was followed by a work-up procedure involving ether extraction, washing of the ether extract with water, and then subsequent drying with magnesium sulfate. Elution chromatography of the product resulted in the isolation of benzophenone and triphenylcarbinol.

Attempted oxidations of the sulfide in non-aqueous solvents yielded only starting sulfide. These included permanganate oxidations in acetone (36), and chromic acid oxidations in ether (37). However, ozonation of the sulfide in chloroform (38), yielded a yellow solid which immediately decomposed on attempted isolation. At least a portion of this decomposed product was identified as benzophenone.

Trityl 4-methylbenzenesulfinat and trityl 2-methylbenzenesulfinat, unlike their analogue the 2,6-dimethyl ester, rearrange in inert solvents to give the corresponding sulfones

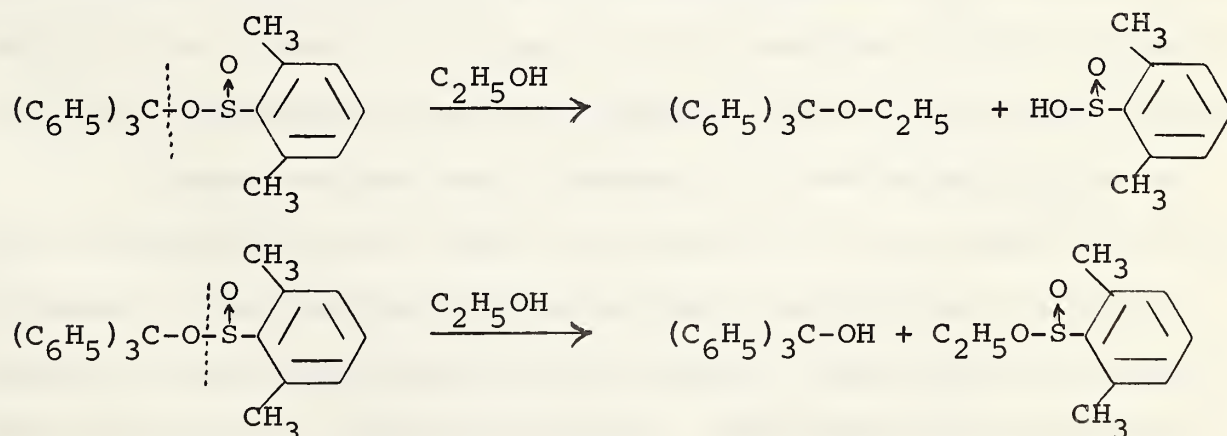
with extreme ease under mild conditions. This becomes very important and has to be guarded against in the synthesis of these esters.

In an attempt to effect a thermal rearrangement of trityl 2,6-dimethylbenzenesulfinate to its sulfone in an inert solvent, solutions of the sulfinate were heated in benzene on the steam bath for seven days, in the presence of 2,6-lutidine. The reaction products were worked-up by extracting with ether, washing with 10% sodium carbonate and water to destroy unreacted ester, followed by drying with magnesium sulfate. The yellow solid obtained after removal of solvent was chromatographed to yield triphenylcarbinol and benzophenone as products. When this reaction was carried out in dioxane, and the products isolated in a similar manner, benzophenone and triphenylcarbinol were again obtained as products. When the sulfinate was heated in acetonitrile on the steam bath for 24 hrs. in the presence of 2,6-lutidine, and the reaction products isolated by washing with water to destroy the unreacted ester and with 10% sodium carbonate to remove acid produced in hydrolysis of the ester, triphenylcarbinol was the only product obtained.

DISCUSSION

The results of these exploratory studies gave some idea of the type of bond-cleavage occurring, and the nature of reactivity of these compounds in solvolysis. These investigations arose from the difficulty encountered in a standard esterification procedure, which has previously been used in the preparation of sulfinate esters (36).

Theoretically, two types of bond cleavage could occur in these systems: (a) Carbon-oxygen bond cleavage, or, (b) Sulfur-oxygen bond cleavage. In order to prevent the latter from occurring, *o*-substituents were used in the acid portion of the molecule, to hinder attack there; but, in any event, the type(s) of cleavage taking place could be readily detected. In ethanolysis, if C-O bond cleavage occurred, trityl ethyl ether and 2,6-dimethylbenzenesulfinic acid would be the only products. However, if S-O bond cleavage took place, then triphenylcarbinol and ethyl 2,6-dimethylbenzenesulfinate would be produced:



The results indicate that C-O bond cleavage occurs in these systems.

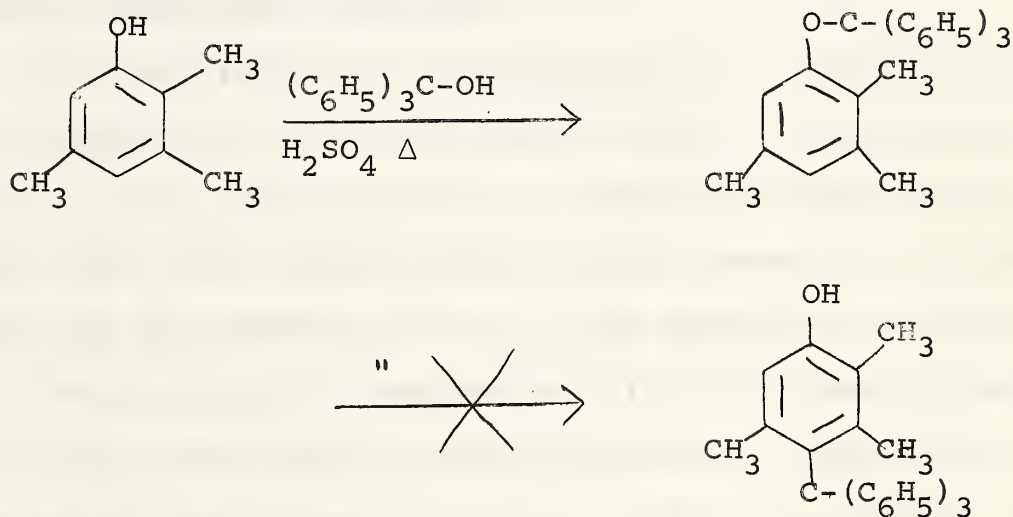
In hydrolysis, no indication of the type of bond cleavage taking place is possible, since the same products, visibly, triphenylcarbinol and 2,6-dimethylbenzenesulfinic acid, would arise

from both types of cleavage. However, the results from Table I indicate how exceedingly reactive these esters are towards water. The role of pyridine in preventing hydrolysis is not clear, but it is possible that this base acts as a buffer to prevent the acid- and base-catalyzed solvolysis of the ester.

The rapidity of the solvolysis of trityl 2-methylphenyl sulfone is noteworthy, since sulfones are generally known to be stable relative to esters, and one might not have expected solvolysis of this compound to occur under these mild conditions. The result becomes interesting when compared with benzhydryl 2,6-dimethylphenyl sulfone, which, under more vigorous reaction conditions (in 80% ethanol-water by volume at 90°C.) does not undergo solvolysis (34). One reason which could be advanced for this observation of the rapid ethanolysis of trityl 2-methylphenyl sulfone, is the generation of the highly stable trityl cation from the substrate system. Furthermore, in the solvolysis of the 2-methyl ester, even if the 2-methyl sulfone was produced, it would not be possible to detect it as a reaction product, since it would have undergone solvolysis itself under the reaction conditions.

Carbon-oxygen bond cleavage of these esters can be an acid-catalyzed process, hence the necessity of the base 2,6-lutidine to prevent this reaction from occurring, and thus give a true measure of the uncatalyzed reaction rate. The results of Table III show how rapid the catalysis can be. The base 2,6-lutidine was selected because of the predicted poor nucleophilicity of the species towards the substrate, which results from the excessive steric requirements associated with the molecule (39). Further support of this was obtained from the results of Swain (15) and

Clark (40). Swain has reported the reaction between trityl halides and tertiary amines to be negligibly slow in benzene, where 4% reaction was observed to occur in six months between trityl bromide and pyridine, while 24% reaction occurred with triethylamine over the same period of time. The results are ascribed to steric hindrance. Clark and co-workers have isolated 2,3,5-trimethylphenyl trityl ether from the reaction of 2,3,5-trimethylphenol with triphenylcarbinol in sulfuric acid. The authors state the reaction site is the oxygen and not the 4-position as previously reported by Hardy (41), because in view of the steric requirements of the trityl cation, it would be quite surprising that such a hindered phenol could be tritylated under the conditions at the 4-position to give 4-triphenylmethyl-2,3,5-trimethylphenol.



Furthermore, Clark has observed that ethyl iodide does not react with 2-triphenylmethylpyridine in nitrobenzene at 60°C. (42). The author states: "It can be concluded with confidence, therefore, that the failure of 2-triphenylmethylpyridine to react with ethyl iodide can be attributed to the steric bulk the triphenylmethyl group provides in the vicinity of the nitrogen atom".

We have found that the trityl cation does react with

2,6-lutidine. This will be discussed later.

The appearance of benzophenone in the non-buffered ethanolysis of the 2,6-dimethyl ester was not rationalized. Further studies are required before any conclusions can be deduced from these observations.

In Table II, the reported yield of trityl ethyl ether and the presence of triphenylcarbinol from the ethanolysis of the 2,6-dimethyl ester in the absence of 2,6-lutidine merit some clarification. One possible explanation for the appearance of triphenylcarbinol here could be the fact that trityl ethyl ether has been observed to undergo acid catalyzed hydrolysis to produce triphenylcarbinol (43). Thus, in the absence of 2,6-lutidine, this reaction could have occurred.

The low yields of triphenylcarbinol in the hydrolysis of the 2,6-dimethyl ester in pentane in Table I, could possibly be due to the low solubility of this compound in this solvent. No control runs with triphenylcarbinol were conducted to determine the extent and the reproducibility of the extraction procedure.

The inability to synthesise trityl 2,6-dimethylphenyl sulfone has been ascribed to steric hindrance. Models show this molecule to be highly hindered in the region of the sulfur atom, and it is quite possible that the o-hydrogens of the triphenylmethyl group interact with those of the methyl groups of the benzene ring rendering the compound unstable and non-isolable. This interpretation is correlated with the observation of the ease of rearrangement of the o- and p-methyl analogues to their sulfones.

In regard to the syntheses of trityl sulfones, no previous record exists in the literature where a trityl sulfone

has been isolated. In 1917 Hinsberg (44) attempted the preparation of trityl α -naphthalenesulfinate in the presence of dilute hydrochloric acid, and isolated a product free from sulfur. Attempts by Gregg (45) to synthesise trityl phenyl sulfone by the chromic acid oxidation of trityl phenyl sulfide in acetic acid, resulted in the production of triphenylcarbinol, diphenyl sulfide and benzenesulfonic acid as products. Djerassi's (46) attempted synthesis of the same sulfone by a ruthenium tetroxide oxidation of trityl phenyl sulfide in carbon tetrachloride yielded triphenylcarbinol and starting sulfide as products. These results may have arisen from the work-up procedure used which involved washing with water and thus affording possible hydrolysis of the sulfone.

EXPERIMENTAL

Reagents

2,6-Lutidine. - Eastman Organic (practical grade) 2,6-lutidine was purified by refluxing with, and distilling from barium oxide. It was stored over potassium hydroxide in a dark screw-capped bottle.

Ethanol. - Absolute ethanol was prepared from commercial 95% ethanol by an initial dehydration with calcium oxide followed by treatment with magnesium ethoxide as described by Fieser (47).

Dioxane. - Purification was effected by use of a method suggested by Fieser (48). Eastman Organic reagent grade dioxane was refluxed with concentrated hydrochloric acid and water for twelve hours under an atmosphere of Nitrogen. The resulting solution was treated with potassium hydroxide and refluxed with sodium, from which it was distilled and stored in dark-coloured screw-capped bottles.

Pentane. - Phillips Petroleum 66 technical grade pentane was purified by refluxing for fifteen hours with, and distillation from, phosphorus pentoxide. The reagent was stored in dark-coloured screw-capped bottles.

Benzene. - Baker and Adamson analytical reagent grade was used.

Diethyl ether. - Mallinckrodt AR absolute ether was used.

Chloroform. - AR Mallinckrodt chloroform was purified by washing with conc. sulfuric acid, and then with water. A preliminary drying was accomplished with anhydrous magnesium sulfate, from which the reagent was filtered into a distilling flask containing phosphorus pentoxide, from which it was distilled. The solvent was stored in the dark in ground glass-stoppered vessels at room temperature, to which Drierite-filled drying tubes were attached. No purified samples were used at a maximum of two days after

purification.

2,6-Dimethylbenzene sulfinic acid (49) - 2,6-Dimethyl aniline (0.232 mole; 28.2 g.) was dissolved in 640 ml. water containing 176 ml. conc. sulfuric acid in a 3-necked flask equipped with a mechanical stirrer. The mixture was cooled to 0°C., using an ice-salt water bath whence white crystals of 2,6-dimethylanilinium sulfate crystallized out. Sodium nitrite (18 g. in 100 ml. water) was added gradually with stirring, and sulfur dioxide bubbled into the reaction mixture for one hour. Copper powder (200 g.) was then added gradually over a 45 min. period, and sulfur dioxide bubbled in overnight (17 hours). The temperature was maintained at 0°C. until after the addition of the copper, but thereafter, allowed to warm up to room temperature. The mixture was filtered, the copper mass washed with cold water, and then extracted with 1000 ml. of 10% sodium carbonate, followed by cooling and acidification of the filtrate with cold 50% sulfuric acid until no more precipitation of the sulfinic acid occurred. The sulfinic acid was then washed with water, air-dried, and stored in the refrigerator. % Yield = 56%; weight = 26.6 g. decomposition temp. = 90 - 91°C.

2,6-Dimethylbenzenesulfinyl chloride (49)- To 0.0224 mole (4.25 g.) of 2,6-dimethylbenzenesulfinic acid in 15 ml. pentane was added 0.053 mole (6.3 g.) thionyl chloride in 10 ml. pentane in a dropwise manner until evolution of gas subsided. The mixture was filtered through glass wool to remove impurities, the receiver containing approximately 0.5 ml. thionyl chloride in pentane. The pentane and excess thionyl chloride were removed by pumping under vacuum overnight to yield a hygroscopic yellow oil. A weight of 4.2 g. corresponded to an 89% yield.

Triphenylcarbinol. - Commercially available Eastman Organic triphenylcarbinol of the highest available purity (m.p. 158-160°C.), was used without further recrystallization.

Trityl 2,6-dimethylbenzenesulfinate. - Preparation was conducted by allowing 0.0675 mole (13.4 g.) of 2,6-dimethylbenzenesulfinyl chloride to react with 0.0338 mole (8.8 g.) of triphenylcarbinol in the presence of pyridine (55 ml.) - the minimum amount necessary for solution of the alcohol.

The pyridine solution of triphenylcarbinol was added to the acid chloride in an ice-methanol bath at -14°C., and the reactants were allowed to remain at this temperature for 30 min. The reaction flask was then transferred to the freezing compartment of the refrigerator at -20°C. for 26 hrs. In the work-up procedure, the contents of the flask were poured into a litre beaker of ice containing 26 ml. of conc. hydrochloric acid, and then thoroughly extracted with ether. The ether layer was washed twice with 70 ml. portions of water, and then twice with 150 ml. portions of 10% sodium carbonate. A final washing with a 100 ml. portion of water gave a pH of 8 in the water layer. The ether solution was then dried over anhydrous magnesium sulfate for 3½ hr. at room temperature. Subsequent evaporation of the ether under an aspirator (with warming of the filter flask with a water bath at 70-80°C.,) resulted in the production of ester contaminated with pyridine. Purification was effected by recrystallization from ether, and a weight of 5.6 g. (m.p. 92-93.5°C.) corresponded to a 41% yield.

Infrared and N.M.R. spectra in carbon disulfide gave positive identification of the compound. In the infrared, strongly-

absorbing bands appeared at 700, 770, 900 and 1135 cm^{-1} , the latter, a characteristic region for sulfinic ester absorption (50).

N.M.R. signals appeared at 2.4 (complex multiplet) and 7.2 τ units (singlet) the former, a region for aromatic proton signals, and the latter, one which has been identified as being associated with the protons of the methyl groups substituted on the benzene ring. The calculated ratio of aromatic to methyl protons of 3:1 agrees fairly well with the found integrated ratio of 3.15:1.

Stability of Ester. - The compound was stored in the refrigerator at deep-freeze temperatures in a tightly stoppered flask. If allowed to sit at room temperature, in a few minutes the white crystalline solid changes colour to yellow. After 47 hrs. at room temperature in a stoppered flask, infrared spectra showed no change from the original material. Nor was any change discernible when the solid was heated on the steam bath for 30 min. However, an attempted chromatography on neutral alumina yielded triphenylcarbinol as the product.

Trityl 2,6-dimethylphenyl sulfide was prepared as previously suggested by Finzi and Bellavita (51) for trityl phenyl sulfide. Triphenylcarbinol (0.0131 mole; 3.4 g.), was dissolved in 40 ml. of warm glacial acetic acid. This solution was treated with 8 ml. of conc. sulfuric acid, and the resulting solution changed from pale yellow to an intense red. To this mixture, 0.0132 mole (1.82 g.) of 2,6-dimethylthiophenol was added dropwise, and the reaction mixture heated on the steam bath. A mass of yellow crystals precipitated from solution, was filtered off in

a sintered-glass funnel, and then washed with glacial acetic acid, and then with ethanol. A weight of 2.1g. (m.p. 145-148°C.) corresponded to a 42% yield. Purification by chromatography on alumina with elution of the sulfide in the pentane fractions, or recrystallization from ether-ethanol yielded a white crystalline product of m.p. 150-151°C.

N.M.R. data: Signals at 2.9 τ units for the aromatic protons and at 7.85 τ for the methyl protons. The found integrated ratio of 1:2.8 agrees with the calculated of 1:3 for methyl protons and aromatic protons. I.R. data: strongly absorbing bands at 700, 730, 770 and 1040 cm^{-1} in addition to the usual C-H stretching at 3000-3100 cm^{-1} .

2-Methylbenzenesulfinic acid. - This acid was prepared by the diazotisation of *o*-toluidine using the same procedure as that for the 2,6-dimethyl acid. Starting with 0.515 mole (55 g.) *o*-toluidine, 69 g. of crude, white, crystalline acid was obtained. The yield on an air-dried basis was 90%; m.p. 70°C. (reported m.p. 80°C. (49)).

2-Methylbenzenesulfinyl chloride was prepared using the procedure previously described for 2,6-dimethylbenzenesulfinyl chloride. Starting with 0.0775 mole (12.0 g.) of 2-methylbenzenesulfinic acid, 0.056 mole (9.76 g.) of acid chloride was obtained, corresponding to a 72% yield.

Trityl 2-methylbenzenesulfinate. - Preparation was conducted by allowing 0.056 mole (9.76 g.) of 2-methylbenzenesulfinyl chloride to react with 0.054 mole (14.0 g.) of triphenylcarbinol in the presence of pyridine (88 ml., 1.09 moles). The pyridine solution of triphenylcarbinol was added to the acid chloride in an ice-methanol bath at -18°C., and the reactants were allowed to remain at this temperature for 30 min. The reaction flask was then transferred to the freezing

compartment of the refrigerator at -20°C . for $3\frac{1}{2}$ hrs. In the work-up procedure, the contents of the flask were poured into a litre beaker containing 35 ml. (0.435 mole) of conc. hydrochloric acid, and then thoroughly extracted with ether. The ether layer was washed twice with 70 ml. portions of water, and then twice with 150 ml. portions of 10% sodium carbonate. A final washing with a 100 ml. portion of water gave a pH of 8 in the water layer. The ether solution was then dried over anhydrous magnesium sulfate for 1 hr. in a flask which was cooled with a water bath at 19°C . Subsequent evaporation of the ether at room temperature yielded ester contaminated with pyridine. Purification was effected by recrystallization from ether (in which, solution of the ester was accomplished at room temperature), and a weight of 8.72 g. corresponded to a 41% yield. An attempted m.p. determination resulted in a colour change from white to yellow at 123°C . with subsequent darkening to brown, and melting with decomposition at $138-139^{\circ}\text{C}$. I.R. data: strongly absorbing bands at 700, 770, 900 and 1135 cm^{-1} in carbon disulfide. N.M.R. data: In carbon disulfide, a singlet at 7.8τ for the o-methyl protons, a complex multiplet at $2.5-3.0\tau$ for the aromatic protons in addition to a quartet at 2.1τ which is assigned to the hydrogen ortho to the ring-carbon adjacent to sulfur. A singlet at 8.15τ is indicative of the methyl protons of the 2-methyl sulfone which is present as impurity. The calculated ratio of aromatic to methyl protons is 6.3:1 and the found integrated ratio is 6.3:1.

The compound was stored in the refrigerator at deep-freeze temperatures in a tightly stoppered flask to prevent decomposition.

4-Methylbenzenesulfinic acid was prepared by the acidification of

the dihydrate of the sodium salt of 4-methylbenzenesulfinic acid (Eastman yellow label 90% Practical grade). The sodium salt (20 g. 0.0935 mole), was dissolved in 20 ml. of water to which dilute sulfuric acid was added until precipitation of the sulfinic acid was complete. After filtration and washing of the precipitate with water, the white solid was allowed to air-dry. A weight of 8 g. (0.0517 mole), of m.p. 87-88 °C. (reported m.p. 85 °C. (52)) corresponded to a 55.5% yield.

4-Methylbenzenesulfinyl chloride was obtained by the reaction of thionyl chloride with 4-methylbenzenesulfinic acid using the procedure described previously for the 2,6-dimethyl acid chloride. Starting with 13 g. (0.084 mole) of acid, 7.3 g. (0.042 mole) of acid chloride was obtained corresponding to a 50% yield.

Trityl 4-methylbenzenesulfinate. - Preparation was conducted by allowing 0.042 mole (7.3 g.) of 4-methylbenzenesulfinyl chloride to react with 0.0378 mole (9.85 g.) of triphenylcarbinol in the presence of pyridine (49 ml.). The pyridine solution of triphenylcarbinol was added to the acid chloride in an ice-methanol bath at -20 °C., and the reactants were allowed to remain at this temperature for 3 min. In the work-up procedure, the contents of the flask were poured into a 600 ml. beaker of ice containing 24 ml. of conc. hydrochloric acid, and then thoroughly extracted with pentane. A heavy white precipitate insoluble in water was left behind after extraction. The pentane solution was then dried over anhydrous magnesium sulfate for thirty minutes in an ice-cooled water bath. Subsequent evaporation of the pentane at room temperature yielded 400 mg. of ester contaminated with triphenylcarbinol (10%) as impurity, but no sulfone. No melting point

was taken and no attempt made to recrystallize this highly reactive compound.

A similar preparation conducted using ether in the extraction procedure, yielded only trityl 2-methylphenyl sulfone as product. I.R. data: strong absorbtion at 700, 770, 900 and 1135 cm^{-1} .

Trityl 2-methylphenyl sulfone was synthesised by the thermal rearrangement of trityl 2-methylbenzenesulfinates in chloroform. Sulfinates (1.0 g.; 0.0275 mole) was dissolved in 20 ml. of chloroform and the solution heated for 30 min. on the steam bath in a round-bottom flask to which a reflux condensor was attached. Evaporation of the solvent yielded a yellow solid, which was recrystallized from chloroform-ether. After recrystallization, a weight of 0.75 g. (0.0206 mole) corresponded to a 75% yield of sulfone m.p. 133.5-135°C.

I.R. data: In carbon disulfide intense absorption was observed at 700, 760, a doublet at 1125, 1145 and a singlet at 1310 cm^{-1} . The latter band is one characteristic of sulfones, and notably absent from sulfinates (50).

N.M.R. data: In carbon disulfide a complex multiplet at 2.5 to 3.3 τ for the aromatic protons, and a singlet at 8.15 τ for the methyl protons. The calculated ratio for aromatic to methyl protons of 6.3 to 1 agrees fairly well with the found integrated ratio of 6.4 to 1.

Apparently melting point is no indication of purity for this compound, since some samples which melted at higher temperatures, were shown by infrared spectra to be less pure than lower-melting samples.

Stability of 2-methyl sulfone. - Relative to the 2-methyl sulfinic acid, the sulfone is fairly stable, although, if exposed to the air for extended periods of time, the white crystalline solid changes colour to yellow, and then to brown. When 0.890 g. (0.0224 mole) of sulfone was chromatographed on 25 g. of neutral alumina, with pentane, followed by benzene as eluants, 0.487 g. (0.0188 mole) of triphenylcarbinol was obtained from the benzene fractions, corresponding to an 80% yield. Triphenylcarbinol was the only material recovered.

Procedures

Solvolysis of the 2-methyl and 2,6-dimethyl esters, and the 2-methyl sulfone in absolute ethanol at room temperature

The experimental details of a particular experiment for trityl 2,6-dimethylbenzenesulfinate will be presented here. A similar procedure was used for the ethanolysis of the 2-methyl sulfinic acid and sulfone at the appropriate concentrations of compounds cited in Table II, and should be applied accordingly.

Trityl 2,6-dimethylbenzenesulfinate, (0.515 g.; 0.00125 mole), was transferred to a 50 ml. volumetric flask containing absolute ethanol and 0.326 g. (0.00152 mole) of 2,6-lutidine. The time required for dissolution was 20 min. The reaction mixture was allowed to sit at room temperature for 2 hr. After this period of time, the reaction mixture was worked-up by pouring the solution into a separatory funnel containing 200 ml. of water and 100 ml. of ether, whence the ethanol was removed by washing the ether extract with eight 150 ml. portions of water. The ether layer was dried with anhydrous magnesium sulfate for 3 hr. at room temperature. After removal of the solvent by evaporation under an aspirator,

0.3175 g. of a pale yellow solid was obtained as crude product. This compound was identified by its IR spectrum to be trityl ethyl ether. (m.p. crude product = 78-80°C.,; reported m.p. (43) 80-81.5°C.). Chromatography of 0.2975 g. of crude product on 9 g. of neutral alumina resulted in the isolation of 0.2901 g. of trityl ethyl ether (m.p. 80-81°C.) in the pentane fractions. The yield of crude ether based on the weight of starting ester (88-95% pure) was 88.5%.

Solvolysis of Trityl 2,6-dimethylbenzenesulfinate in Ethanol-water

The ester (0.105 g.) was dissolved in 10 ml. of absolute ethanol. A period of 5 min. was required for the ester to dissolve, and the reaction mixture was allowed to sit at room temperature for a further 5 min. After this period a 5 ml. aliquot of this solution was removed and added to 20 ml. of boiled distilled water, which had been previously titrated to a pink phenolphthalein end point with 0.0385 M. sodium methoxide. Titration of this solution required 3.14 ml. of 0.0385 M. sodium methoxide.

To the second 5 ml. portion of ester in ethanol, 20 ml. of boiled distilled water (previously titrated to a pink phenolphthalein end point) was added, and titration of the reaction mixture done immediately. The volume of 0.0385 M. sodium methoxide required was 3.125 ml. The total time which elapsed between addition of the ester and titration of this solution was 15 min.

From the total volume of base used, the calculated percentage of acid produced was found to be 94.63%.

Chromatography of reaction products from ethanol-water solvolysis.

The titrated solutions were combined and extracted with ether. Subsequent drying over anhydrous magnesium sulfate, and

evaporation of the solvent under an aspirator tube, yielded 0.0715 g. of crude product. This was chromatographed on 2.25 g. of neutral alumina to yield 0.0676 g. of trityl ethyl ether in the pentane fractions. No other products were obtained in later fractions. This weight corresponds to a 68% yield based on weight of starting ester.

Solvolysis of Trityl 2,6-dimethylbenzenesulfinate in Dioxane-water.

The ester (0.100 g.,; 0.000244 mole) was dissolved in 10 ml. of dioxane and allowed to sit at room temperature for 15 min. before a 5 ml. aliquot of this solution was removed and added to 20 ml. of boiled distilled water (titrated to a pink phenolphthalein end point). Titration with 0.0385 M. sodium methoxide required 2.670 ml. of titrant. After one hour, complete discharge of the pink colour was observed to occur, and a further 0.14 ml. of base was required to bring the solution back to neutrality. Thus, a total of 2.81 ml. of base was required to neutralize all of the acid produced within 1 hr. after adding the water.

Thirty minutes after dissolving the ester in dioxane, 20 ml. of water was added to the second 5 ml. portion of ester solution. Titration of the reaction mixture required 2.50 ml. of base. Thirty minutes later, this solution required a further 0.30 ml. of base to bring the solution to neutrality. Thus, a total of 2.80 ml. of base was required to neutralize all of the acid produced within thirty minutes after adding the water.

A volume of 2.80 ml. of 0.0385 M. sodium methoxide for each 5 ml. aliquot corresponds to an 86% yield of acid, based on weight of starting ester.

Hydrolysis of solutions of trityl 2,6-dimethylbenzenesulfinate

A typical procedure will be cited here, using the hydrolysis of the ester in pentane with water, hydrochloric acid and sodium carbonate as additives for an example. The concentrations of the various additives used here are the same as those used when chloroform, benzene and ether were employed as solvents.

The sulfinate (0.221 g.) was dissolved in 40 ml. of pentane. This solution was added to, and shaken with 7 ml. of 1 N hydrochloric acid in a separatory funnel. This was followed by the addition of, and shaking with two 30 ml. portions of water, followed by a washing with 5 ml. of 10% sodium carbonate. A final washing with two 30 ml. portions of water resulted in a pH of 7 in the water layer. Drying of the pentane with anhydrous magnesium sulfate, and subsequent evaporation of the solvent under an aspirator, yielded 0.0771 g. of triphenylcarbinol of m.p. 151-156°C., (reported m.p. 162° C. (53)) which was identified by its IR spectrum. No starting ester or other reaction products were found to be present.

Permanganate oxidation in acetic acid (35).

Trityl 2,6-dimethylphenyl sulfide (5.0 g.; 0.0142 mole) was dissolved in 100 ml. of glacial acetic acid by warming on the steam bath. This solution was treated with 2 ml. aliquots of a 3% aqueous solution of potassium permanganate, and the mixture vigorously stirred with a mechanical stirrer. The permanganate was added as fast as the purple colour was discharged (approximately 45 min. intervals). When no further decolourization occurred, the excess permanganate was removed by treatment with a solution of sulfurous acid, and the reaction mixture then poured into a

600 ml. beaker of ice. The precipitated product was filtered off and recrystallized from ethanol to yield 2.764 g. of starting sulfide of m.p. 143-145°C.

Hydrogen peroxide oxidation in acetic acid.

Trityl 2,6-dimethylphenyl sulfide (1.06 g.; 0.003 mole) was dissolved in 100 ml. of glacial acetic acid by warming on the steam bath. To this solution 1 ml. of 30% aqueous hydrogen peroxide was added, and the reaction mixture was vigorously stirred at room temperature for 24 hrs. After this period of time the solution was extracted with an ether-water mixture, followed by drying of the ether layer with anhydrous magnesium sulfate, and subsequent removal of the solvent by evaporation under an aspirator tube. A yield of 0.5443 g. of crude product was obtained. Chromatography on neutral alumina yielded 0.279 g. of benzophenone in the pentane fractions, and 0.089 g. of triphenylcarbinol in the benzene fractions, corresponding respectively to 96% and 12.2% yields based on weight of starting sulfide.

Permanganate oxidation in acetone (36).

Trityl 2,6-dimethylphenyl sulfide (1.0 g.; 0.00284 mole) was dissolved in 90 ml. of acetone, and a 50-50 (by weight) finely ground mixture of potassium permanganate and magnesium sulfate was added periodically. At approximately 1 hr. intervals, the violet colour was observed to be discharged, and more oxidant was added. Aliquots of reaction mixture were removed at 1, 8, and 22 hr. intervals. These were treated in the same manner, that is, the brown manganese dioxide precipitate was filtered off and the acetone evaporated under an aspirator to yield starting sulfide of m.p. 154-156°C. The weight of the product was not recorded.

Chromic acid oxidation in ether

The method suggested by Brown (37) was used here in the specified proportions, following the specific procedure. Starting with 1 g. (0.00284 mole) of trityl 2,6-dimethylphenyl sulfide starting material was obtained as the product.

Ozonation in chloroform (38)

Trityl 2,6-dimethylphenyl sulfide (0.373 g.; 0.00106 mole) was dissolved in 10 ml. of chloroform, and ozone bubbled into the solution for 4 hr. to yield a yellow flocculent precipitate which was filtered off in a sintered-glass funnel. This immediately decomposed to a brown, viscous mass on exposure to the air. On evaporation of the solvent from the filtrate, the same yellow, decomposable material was again obtained. No weighings were taken. IR spectra of the decomposed product in carbon disulfide showed at least part of the product to be benzophenone.

Reaction Products

Triphenylcarbinol was identified by its IR spectrum.

Trityl 4-methylphenyl sulfone resulted from the rearrangement of the 4-methyl sulfinic acid in attempted syntheses of this compound, using ether as extracting solvent in the work-up procedure instead of pentane. In an attempted preparation of the ester, from 7.05 g. of 4-methylsulfinic acid and 5.3 g. of triphenylcarbinol, which should have yielded 8.5 g. of ester as product, 6.4 g. of sulfone was obtained, corresponding to a 75% yield. The crude product melted at 163-164°C. IR data: In carbon disulfide, intense absorption was observed at 700, 760, 810, 1035, 1165 and 1380 cm.⁻¹.

Benzophenone was identified as a reaction product from its I.R. and N.M.R. spectra, which were identical to an authentic sample of benzophenone (m.p. product 45-46°C.; m.p. benzophenone 43-45°C.; mixed m.p. 44-46°C.).

Trityl ethyl ether was synthesised by the method suggested by Norris and Young (43) for the reaction of trityl chloride with sodium ethoxide. Starting with 2.47 g. (0.00890 mole) of trityl chloride (Matheson Coleman white label m.p. 109-111°C.), 2.4 g. (0.00835 mole) of trityl ethyl ether of m.p. 78-80°C. was obtained, corresponding to a 92.5% yield. One recrystallization from ether yielded 1.756 g. of material melting at 80-81.5°C. (reported m.p. 81.3°C.) An I.R. spectrum of the material revealed intense bands at 700, a triplet at 750, 760, 775 and a singlet at 1050 cm.^{-1} .

Trityl ethyl ether obtained as a reaction product, was identified by a comparison of its I.R. spectrum with that of an authentic sample. The spectra were found to be superimposable.

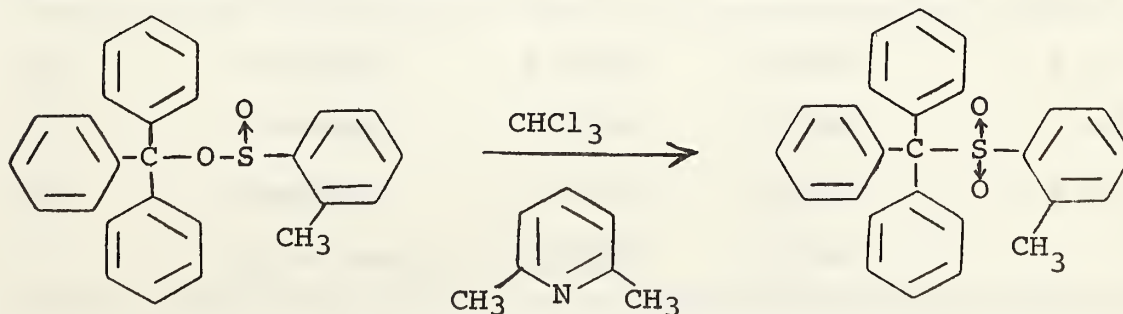
CHAPTER II

Rearrangement and Substitution Processes in Solvents of Low
Dielectric Constant

Having realized that the rates of concurrent solvolysis and rearrangement of trityl arenesulfinates were immeasurably fast in ethanol at room temperature, it was decided to study the rearrangement and substitution reactions of the esters in low dielectric constant solvents, in the hope that these reactions might proceed at a measurable rate in these solvents. Among the requirements which became important in the selection of solvents for this purpose, was: (a) high solubility of these esters in the solvent, and (b) the solvent should have a high degree of purity in order to prevent reactions of the substrate systems with impurities from occurring. Chloroform and carbon tetrachloride presented themselves as logical choices over pentane, benzene and ether, since the esters were found to have relatively high solubility in these solvents.

RESULTS

The observed rate of rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone at 25°C. in chloroform, with 2,6-lutidine present as base, was found to be a first-order process.



The rearrangement is first order with respect to the sulfinic ester, and $k_{ob.}$ is $5.57 \pm 0.07 \times 10^{-4} \text{ sec.}^{-1}$. A plot of $\log (a-x)$ versus time showed good linearity. Such a typical plot is presented in Fig. I. Trityl 2-methylphenyl sulfone was the only product of the reaction. When the concentration of the 2-methyl ester was increased from 0.025 M. to 0.075 M., no significant change in the observed rate of rearrangement was apparent, ($k_{ob.} = 6.42 \pm 0.13 \times 10^{-4} \text{ sec.}^{-1}$), and the linearity in the plot of $\log (a-x)$ versus time was maintained (Fig I). These results are given in Table IV.

The least hindered of the three esters at the sulfur atom, the *p*-substituted ester, trityl 4-methylbenzenesulfinate, rearranged to trityl 4-methylphenyl sulfone under similar conditions to those of the *o*-methyl substituted ester with an observed first-order rate of $9.68 \pm 0.27 \times 10^{-4} \text{ sec.}^{-1}$. But, under similar reaction conditions, the most hindered of the three esters, visibly, trityl 2,6-dimethylbenzenesulfinate, did not rearrange to its corresponding sulfone even after several months. These data are illustrated in Table IV.

Table IV

The rearrangement of some Trityl arenesulfinates in chloroform at 25°C.

Run	Trityl benzene sulfinate	M.	2,6-lutidine (M.)	$k_{ob.} \times 10^4 (\text{sec.}^{-1})$
11	2-methyl	0.0250	0.0306	5.57 ± 0.07
12	2-methyl	0.0750	0.0306	6.42 ± 0.13
10	4-methyl	0.0250	0.0306	9.68 ± 0.27
9	2,6-dimethyl	0.0250	0.0306	- ^a

^a No sulfone was detectable after four months.

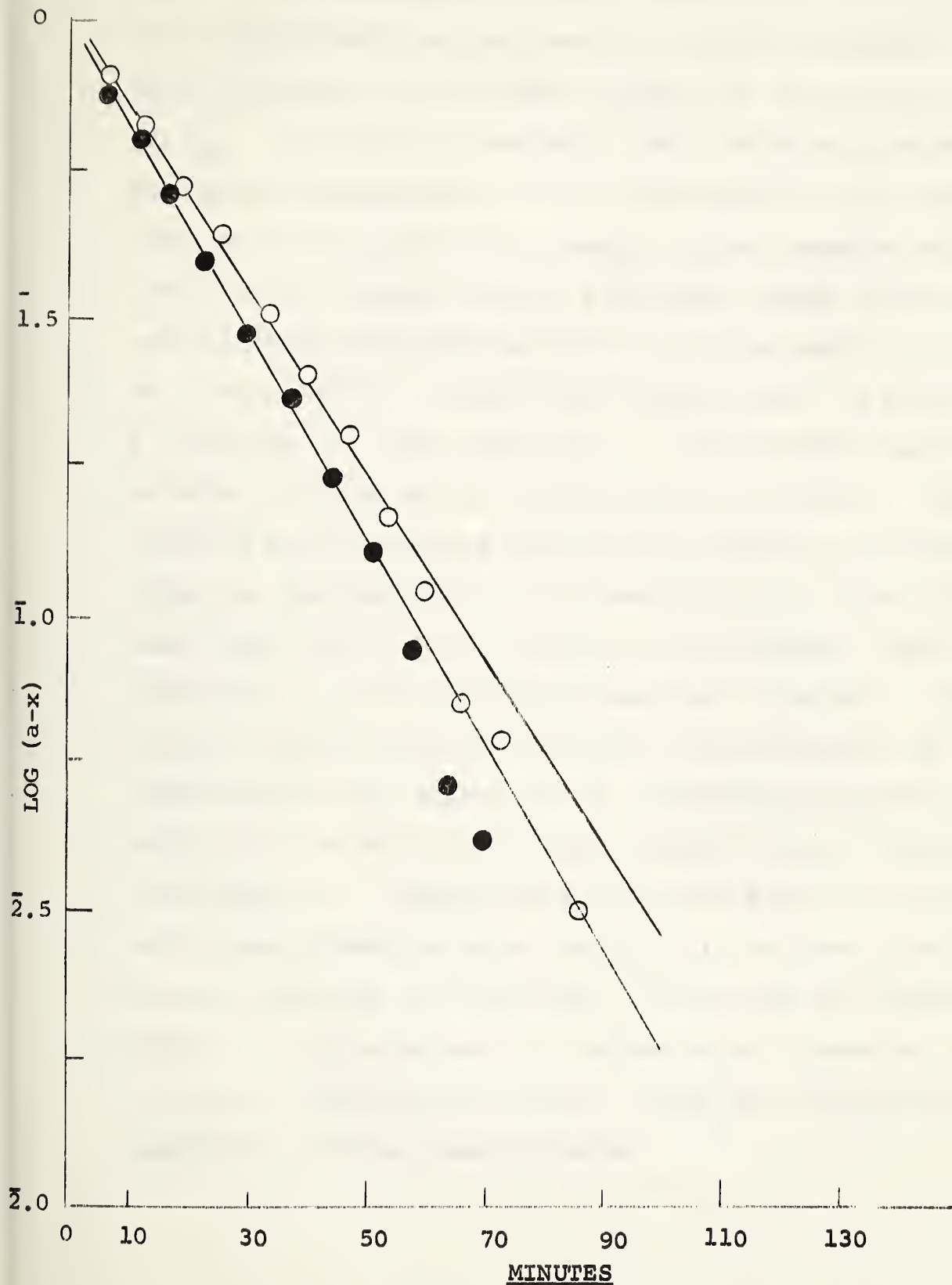


Fig. I Plot of decrease in concentration of ester versus time for the rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone (0.02 M, Run # 11 = ○; 0.075 M. Run # 12 = ●).

At this point it would probably be best to illustrate some factors which become important in the determination of these rate constants, and to give an example of the method of calculation of k_{ob} . In the first instance, these rates were conducted by following the appearance of the sulfone band in the infrared. This was done by injecting a sample of the reaction solution into a 0.5 mm cell matched against a variable spacer type reference cell, and following the appearance of the sulfone band at 7.73 microns on a Perkin Elmer instrument by scanning over the range 7.30 to 8.1 microns, at room temperature. The recorded time was that at which the apex of the sulfone peak was reached. Thus, if the starting ester contained sulfone as an impurity, this had no effect on the reaction, or the reaction rate, since the sulfones were found to be inert, (relative to the esters), under these conditions. Nor does triphenylcarbinol interfere. However, should a base be absent, and prevent neutralization of minute, undetectable trace quantities of 2,6-dimethylbenzenesulfinic acid, which might be present, the rearrangement occurs extremely rapidly (see Table V). Whether the base involved was 2,6-lutidine or tetra-n-butylammonium azide, essentially the same rate of rearrangement was observed in chloroform. These data are presented in Table V. The acid-catalytic nature of this reaction, and evidence to show how these bases interact, or do not interact, with the substrate, will be discussed later.

Table V.

The effect of Bases on the rate of rearrangement of Trityl
2-methylbenzenesulfinate in chloroform at 25°C.

Run	Sulfinate (M.)	Base	(M.)	$k_{\text{ob.}} \times 10^4 (\text{sec.}^{-1})$
11	0.0250	2,6-lutidine	0.0306	5.57 ± 0.07
54	0.0250	--	-	- ^a
56	0.0255	(<u>n</u> -Bu) ₄ N azide	0.0127	6.03 ± 0.16

^a Rapid quantitative production of sulfone resulted.

A linear relationship resulting from a plot of concentration versus absorbance for trityl 2-methylphenyl sulfone in chloroform, showed adherence to the Lambert-Beer law. Such a plot is presented in Fig. II. This compound, however, was observed to gradually disappear over extended periods of time. After 167 hrs. at room temperature in chloroform, the absorbance of the sulfone band in the infrared for a 0.0250 M. solution decreased from 0.2509 to 0.1672, that is, by 0.0837 absorbance units (see Table VI). Nevertheless, it should be noted that this disappearance does not significantly affect the sulfone concentration measured in the rearrangement of the 2-methyl ester, since 5 hrs. represents a 10 half-life period for this reaction.

An illustration of the type of rate calculation involved is given in Table VII.

Chloroform was selected as solvent over carbon tetrachloride because of the rapid, yet easily measurable rates which could be conducted at room temperature.

Fig. II Lambert-Beer law plot for Trityl 2-methylphenyl
sulfone in chloroform

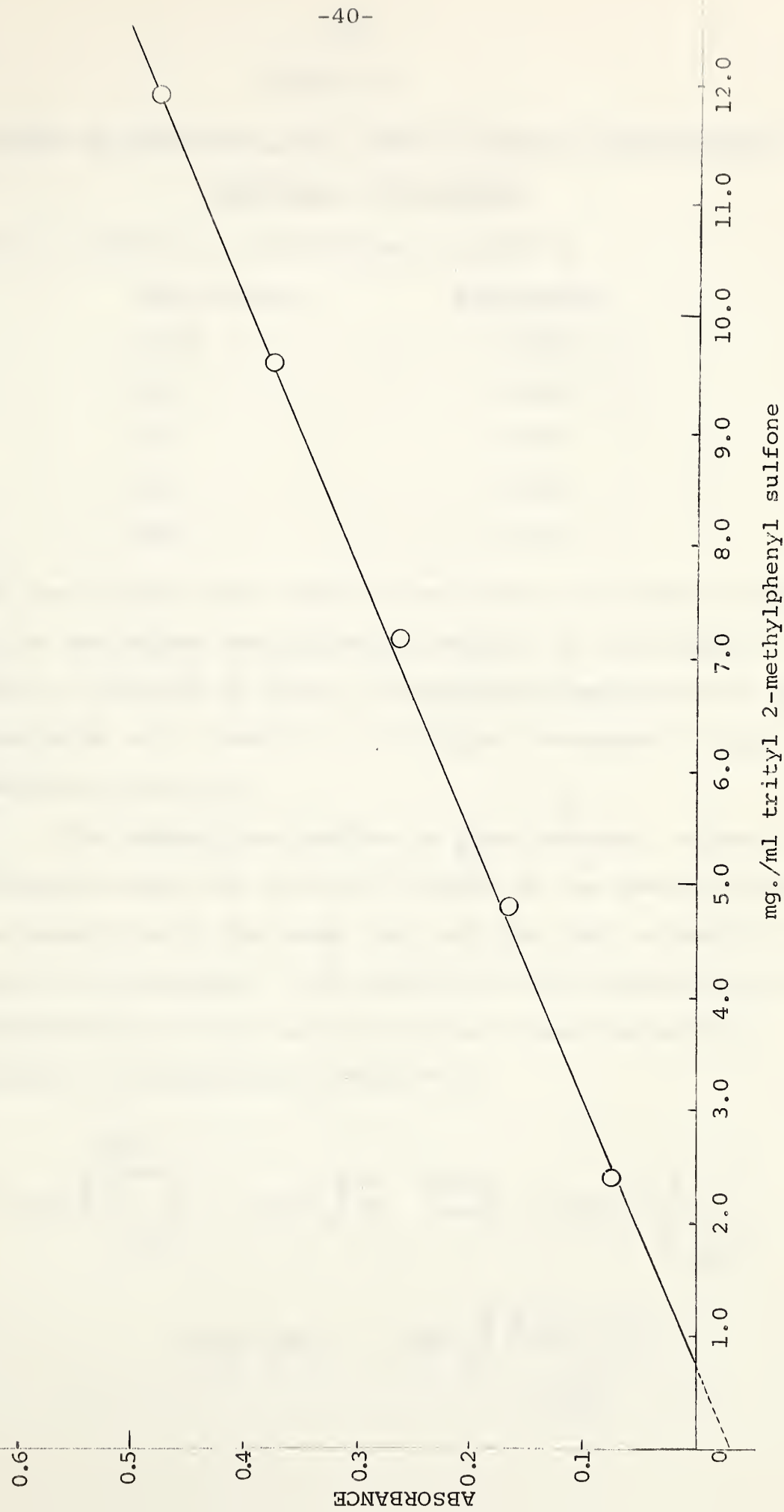


Table VI.

The change of Absorbance with Time for Trityl 2-methylphenyl sulfone in chloroform

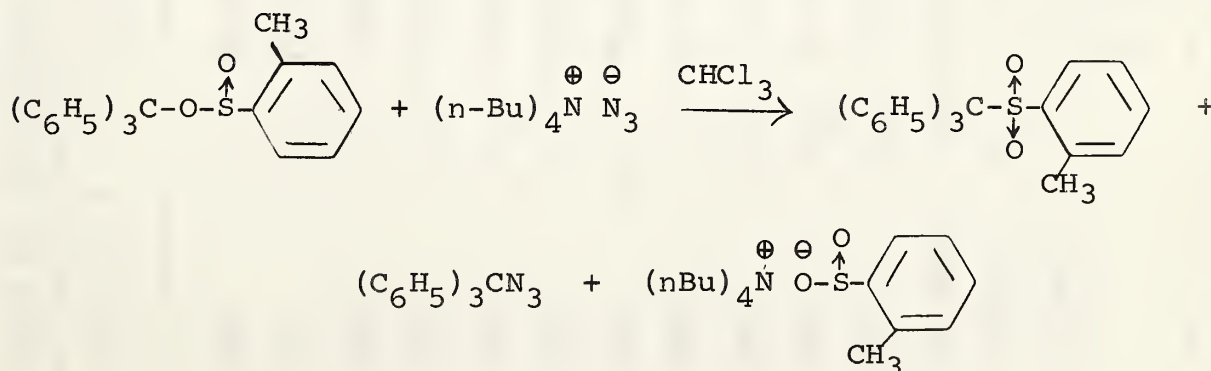
Sulfone = 0.0250 M.; 2,6-lutidine = 0.0358 M.

<u>Time</u> (hours)	<u>Absorbance</u>
0.07	0.2509
24	0.2382
72	0.2057
119	0.1836
168	0.1672

All of these esters were found to be relatively stable in carbon disulfide and carbon tetrachloride compared to chloroform.

A 0.0250 M. solution of trityl 2-methylbenzenesulfinate in carbon tetrachloride with 0.0285 M. 2,6-lutidine rearranged to give 51% sulfone in 66½ hrs.

For competition studies in these systems, tetra-n-butylammonium azide was selected because of the powerful nucleophilic properties of the azide ion, and the ready solubility of this salt in chloroform. The results of the reactions of trityl 2-methylbenzenesulfinate and tetra-n-butylammonium azide in chloroform are summarised in Table VIII.



Calculations for the determination of k_{ob} in the rearrangement of trityl 2-methylbenzene-

sulfinate in chloroform at 25°C. with added 2,6-lutidine

Run # 12 [Sulfinate] = 0.075 M. ; [2,6-lutidine] = 0.0306 M.

Time(sec.)	$A_{ob.} (\log I_0/I)$	$A_{ob.}/A_{\infty}$	(a-x)	$\log(a-x)$	$\log(a_0/a-x)$	$k_{ob} \times 10^4$ (sec. ⁻¹)
369	t_1	89.7/48.2 = 0.2698	0.2471	0.7529	1.8767	-
714	t_2	89.7/34.8 = 0.4112	0.3765	0.6235	1.7948	5.45
1039	t_3	88.8/25.2 = 0.5470	0.5009	0.4991	1.6982	6.13
1398	t_4	89.0/19.0 = 0.6706	0.6142	0.3857	1.5863	6.47
1740	t_5	88.1/15.1 = 0.7660	0.7015	0.2984	1.4748	6.55
2220	t_6	88.1/12.7 = 0.8412	0.7703	0.2296	1.3610	6.32
2661	t_7	88.1/11.5 = 0.8843	0.8287	0.1712	1.2335	6.45
3085	t_8	87.4/9.7 = 0.9547	0.8742	0.1257	1.0993	6.60
3493	t_9	87.5/8.8 = 0.9975	0.9131	0.0868	2.9385	6.90
3830	t_{10}	87.0/8.0 = 1.0364	0.9486	0.0513	2.7101	7.75
4199	t_{11}	87.8/7.9 = 1.0459	0.9579	0.0420	2.6232	7.55
200 min.	t_{12}	87.1/7.3 = 1.0767	0.9865	0.0134	2.1271	-
239 min.	t_{13}	87.1/7.0 = 1.0949	-	-	-	-
279 min.	t	Average = 1.0919 of 3 values (1.0899, 1.0934, 1.0924)	1.0000	-	-	-

k_{ob} for points before 5% and after 90% reaction were discarded, giving an av. $k_{ob} = 6.42$
 $\pm 0.13 \times 10^{-4}$ sec.⁻¹.

Table VIII.

The substitution of trityl 2-methylbenzenesulfinate with tetra-n-butylammonium azide
in chloroform at 25°C.

Run	t_{∞} (min.)	Ester (M.)	Azide (M.)	2,6- lutidine (M.)	% Trityl azide	% Sulfone ^a	$k_{ob.} \times 10^4$ (sec. ⁻¹)	$k_{Tr.az.} \times 10^6$ (sec. ⁻¹)	$k_{Tr.az.} \times 10^3$ (l./mole sec)
22	191	0.0109	0.0109	0.0302	2.51	97.49	5.80 ± 0.18	14.55	1.33
^b 20	148	0.0257	0.0256	0.0295	5.75	94.25	5.16 ± 0.40	29.6	1.16
23	187	0.0234	0.0134	0.0311	4.12	95.88	5.86 ± 0.25	24.2	1.81
24	189	0.0235	0.0248	0.0311	7.26	92.74	6.07 ± 0.09	44.2	1.78
25	186	0.0235	0.0455	0.0311	12.00	88.00	9.14 ± 0.33	110	2.42
31	34	0.0232	0.2060	0.0310	46.50	53.50	14.70 ± 0.05	685	3.32
56	120	0.0255	0.0127	-	2.06	97.94	6.03 ± 0.16	12.4	0.97
Ethanol									
14		0.0250	0.0533	0.0298	-	100	5.71 ± 0.18	-	-

^a Obtained by difference.

^b Appearance of trityl azide measured.

The rearranged product, the 2-methyl sulfone, and the substitution products, trityl azide and tetra-n-butylammonium 2-methylbenzenesulfinate, were the only products of the reaction. On examining Table VIII, it is apparent that at a constant concentration of 2-methyl ester, the percentage of trityl azide produced increases, and the percentage of 2-methyl sulfone decreases, as the concentration of tetra-n-butylammonium azide is increased relative to ester. When the concentration of ionic azide is increased by a factor of 16 (0.013 M. to 0.206 M.), k_{ob} does not change by more than a factor of 2.5 (5.86×10^{-4} to 14.7×10^{-4}).

These rates measure the disappearance of ester. k_{ob} is a first order rate which gives a measure of $\frac{d[\text{sulfone}]}{dt} + \frac{d[\text{trityl azide}]}{dt}$. The rate of formation of sulfone has already been established to be first order with respect to ester. From Table VIII, it can be seen that the rate of formation of trityl azide is a second-order process, since calculated second-order rate constants from k_{ob} remain fairly constant over a wide concentration range of ionic azide, whereas, calculated first-order rate constants vary by a factor of 28 (24.2×10^{-6} to 685×10^{-6}), in varying the concentration of ionic azide sixteenfold.

When the nucleophile was ethanol, no trityl ethyl ether was produced, and the rate of sulfone formation remained unaffected (Table VIII).

Trityl 2,6-dimethylbenzenesulfinate does not rearrange to give the corresponding sulfone, (Table IV), but does exchange with tetra-n-butylammonium azide in chloroform. The formation of trityl azide is an overall second order process. The first order rate constant increased by a factor of eleven when the concentration

of ionic azide was varied by a factor of seven, but the calculated second order rate did not change by more than a factor of two over this concentration range. These data are given in Table IX.

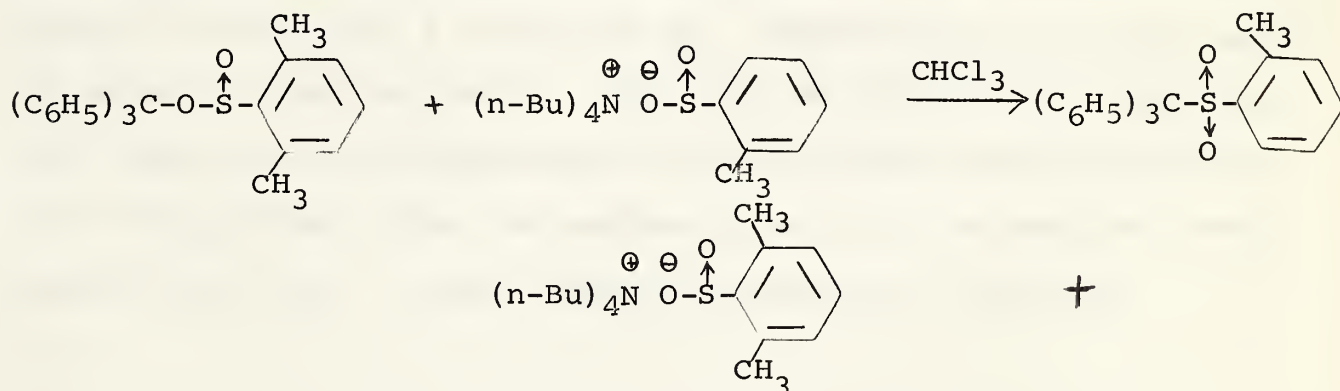
Table IX.

The substitution of trityl 2,6-dimethylbenzenesulfinate with tetra-*n*-butylammonium azide and 2-methyl sulfinate salts in chloroform at 25°C.

Run	Ester		2,6-lutidine (M.)	(<i>n</i> -Bu) ₄ N azide (M.)	(<i>n</i> -Bu) ₄ N sulfinate (M.)	<i>k</i> _{ob} × 10 ⁶ (sec. ⁻¹)	<i>k</i> ² × 10 ⁴ (l./moles sec)
21	0.0297	-	0.0295	0.0297	-	7.55 ± 0.80	2.54
42	0.0297	-	0.0296	0.2040	-	83.60 ± 0.61	4.10
16	0.0252	-	0.0299	-	0.0252	- ^a	

^a 25.2% 2-methyl sulfone was produced after 46 hrs.

On changing the nucleophile to tetra-*n*-butylammonium 2-methylbenzenesulfinate, for the 2,6-dimethyl ester, trityl 2-methylphenyl sulfone was isolated as the product.



A mixed melting point with an authentic sample of this compound showed no depression in melting, and the rate of 2-methyl sulfone formation was found to be approximately one-third as fast as that for trityl azide formation, at the same concentrations of 2,6-dimethyl ester, ionic azide, and ionic sulfinate. The calculations are given in the Discussion section. This rate was not followed

to completion because of its slow nature, complicated with the fact that the 2-methyl sulfone disappears in chloroform over long periods of time as shown above.

The appearance of trityl azide was followed in Runs # 21 and 42, and no problems arise here since trityl azide is stable under the reaction conditions, and no sulfone is produced. An example of the rate calculation involved is given in Table X. The runs involving the 2-methyl ester measure the appearance of the 2-methyl sulfone, and the rate calculation for k_{ob} is based on the maximum amount of sulfone generated in a run. After this value has been determined, the trityl azide band is then checked. In this way, the amount of sulfone produced by rearrangement of the ester in the presence of ionic azide, and the amount of trityl azide which resulted while this process was occurring can be determined. It was believed that tetra-n-butylammonium azide could possibly react with the 2-methyl sulfone to generate trityl azide, and thus give a value for the concentration of trityl azide in excess of the true value. In order to determine how important this might be, the disappearance of the sulfone band was followed for several hours after the maximum quantity of sulfone had been produced in a run. These data are presented in Table XI.

Table X.

Calculations for the determination of $k_{ob.}$ in the substitution of trityl 2,6-dimethylbenzene-sulfinate in chloroform at 25°C. with added 2,6-lutidine.

Run # 42 [Sulfinate] = 0.0297 M.; [(n-Bu)₄Nazide] = 0.204 M.; [2,6-lutidine] = 0.0296 M.

Time (min.)	$A_{ob.}(\log I_0/I_1)$	$A_{ob.}(\text{mg./ml.})$	(a-x)	$\log(a-x)$	$\log(ao/a-x)$	$k_{ob.} \times 10^5 \text{ sec.}^{-1}$
t_1 5	0.0350	0.15	8.45	0.9269	0.0076	Let $t_1=t_o$ then:
t_2 11	0.0618	0.32	8.28	0.9180	0.0165	Time (min) $\log(ao/a-x)$ $k \times 10^5 \text{ sec.}^{-1}$
t_3 17	0.0987	0.57	8.03	0.9047	0.0298	6 0.0089 5.70
t_4 24	0.1403	0.87	7.73	0.8882	0.0463	12 0.0222 7.10
t_5 29	0.1644	1.05	7.55	0.8779	0.0566	19 0.0387 7.80
t_6 34	0.2078	1.37	7.23	0.8591	0.0754	24 0.0490 7.82
t_7 38 $\frac{1}{2}$	0.2255	1.50	7.10	0.8513	0.0832	29 0.0678 8.96
t_8 44	0.2442	1.65	6.95	0.8420	0.0925	33 $\frac{1}{2}$ 0.0756 8.80
t_9 47	0.2677	1.90	6.70	0.8261	0.1084	39 0.0849 8.35
t_{10} 50	0.2854	2.0	6.60	0.8195	0.1150	42 0.1008 9.15
t_{11} 55 $\frac{1}{2}$	0.3054	2.15	6.45	0.8096	0.1249	45 0.1074 9.15
t_{12} 61	0.3389	2.42	6.18	0.7910	0.1435	50 $\frac{1}{2}$ 0.1173 8.93
t_{13} 67	0.3680	2.65	5.95	0.7745	0.1600	56 0.1359 9.15
t_{14} 73	0.3780	2.75	5.85	0.7672	0.1673	62 0.1524 9.45
t_{15} 83	0.4185	3.10	5.50	0.7404	0.1941	68 0.1597 9.00
						78 0.1865 9.16

t_{16}	$94\frac{1}{2}$	0.4667	3.47	5.13	0.7101	0.2244	$89\frac{1}{2}$	0.2168	9.30
t_{17}	$103\frac{1}{2}$	0.4919	3.67	4.93	0.6928	0.2417	$98\frac{1}{2}$	0.2341	9.10
t_{18}	117	0.5279	4.00	4.60	0.6628	0.2717	112	0.2641	9.05
t_{19}	$132\frac{1}{2}$	0.5586	4.27	4.33	0.6365	0.2980	$127\frac{1}{2}$	0.2954	8.75
t_{20}	182	0.6465	5.10	3.50	0.5441	0.3904	177	0.3828	8.30
t_{21}	287	0.8017	7.05	1.55	0.1903	0.7442	282	0.7366	10.00
t_{22}	429	0.7345	6.17	2.43	0.3856	0.5489	-	-	-
t_{23}	20hrs. 9min.0.8992		8.60	-	-	-	-	-	-
$t_{24}=t_{\infty}$	25hrs. 35min.0.900		8.60	-	-	-	-	-	-

Average value of $k_{ob.} = 8.36 \pm 0.61 \times 10^{-5} \text{ sec.}^{-1}$

Table XI.

Changes of Absorbance with time for the reaction of Tetra-n-butylammonium azide with Trityl 2-methylphenyl sulfone in chloroform at 25°C.

Run	(n-Bu) ₄ N ⁺ azide (M.)	Sulfinate (M.)	2,6- lutidine (M.)	Time (hr.)	Absorbance (sulfone)
22	0.0109	0.0109	0.0302	3.06	0.1639
				4.10	0.1602
				5.0	0.1619
				7.35	0.1562
31	0.2060	0.0232	0.0310	0.56	0.1792
				1.0	0.1788
				4.5	0.1549
				6.8	0.1539
				7.9	0.1529

In run 22, the maximum quantity of sulfone was produced in 3.06 hr. Four hours later, the sulfone absorbance was observed to have been reduced by 0.007 absorbance units (from 0.1639 to 0.1562). In run 31, after 34 min. the maximum amount of sulfone was generated, and had an absorbance of 0.1792. Eight hours later, the value had reduced by 0.0265 absorbance units to an absorbance of 0.1529. These changes are within experimental error, and therefore suggest that any error introduced in the measurement of the sulfone and trityl azide absorbances by the reaction of the sulfone with ionic azide become insignificant.

It should be pointed out here, that whereas trityl azide absorbs at 4.8 microns in the infrared, tetra-n-butylammonium azide absorbs at 5.3 microns. Consequently, when necessary, the appearance of trityl azide and the disappearance of ionic azide

may be followed at the same time in a given run. However, in view of the intense absorption of the ionic azide at small concentrations, errors in measurement tend to be greater when its disappearance is being measured, than when the appearance of trityl azide is measured. Neither trityl azide nor tetra-n-butylammonium azide obey the Lambert-Beer law in chloroform (see Figs. V and VI). An illustration of the calculation of the rate constant when the trityl azide band is followed is given in Table XII. An example is also given for a run conducted in acetonitrile in Table XIII. The methods which have been described here were also used in solvents of high dielectric constant, and since these methods will not be discussed in later chapters, it is probably best to cite an example from those results here.

Fig.III Lambert-Beer law plot for Trityl azide in chloroform.

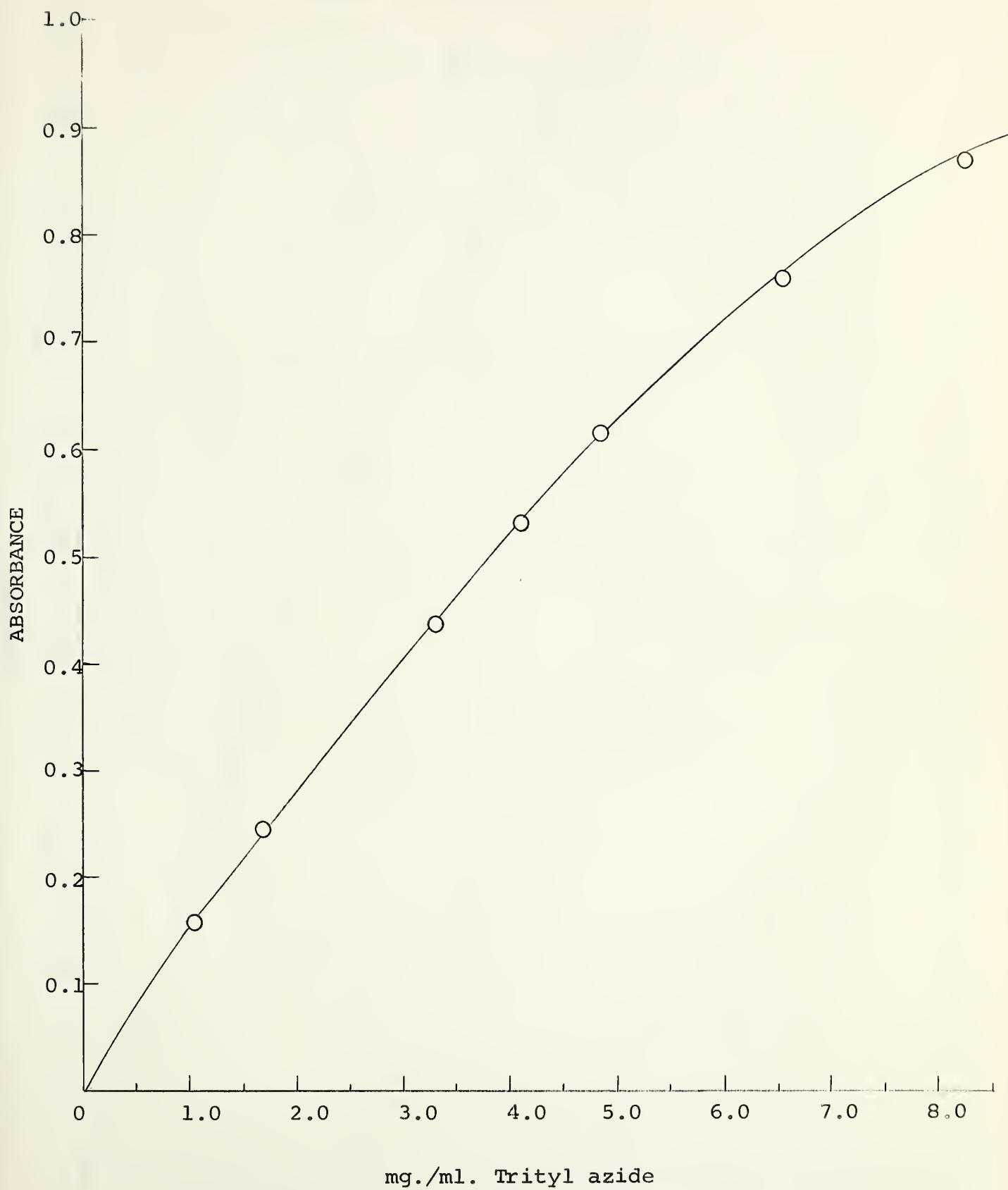
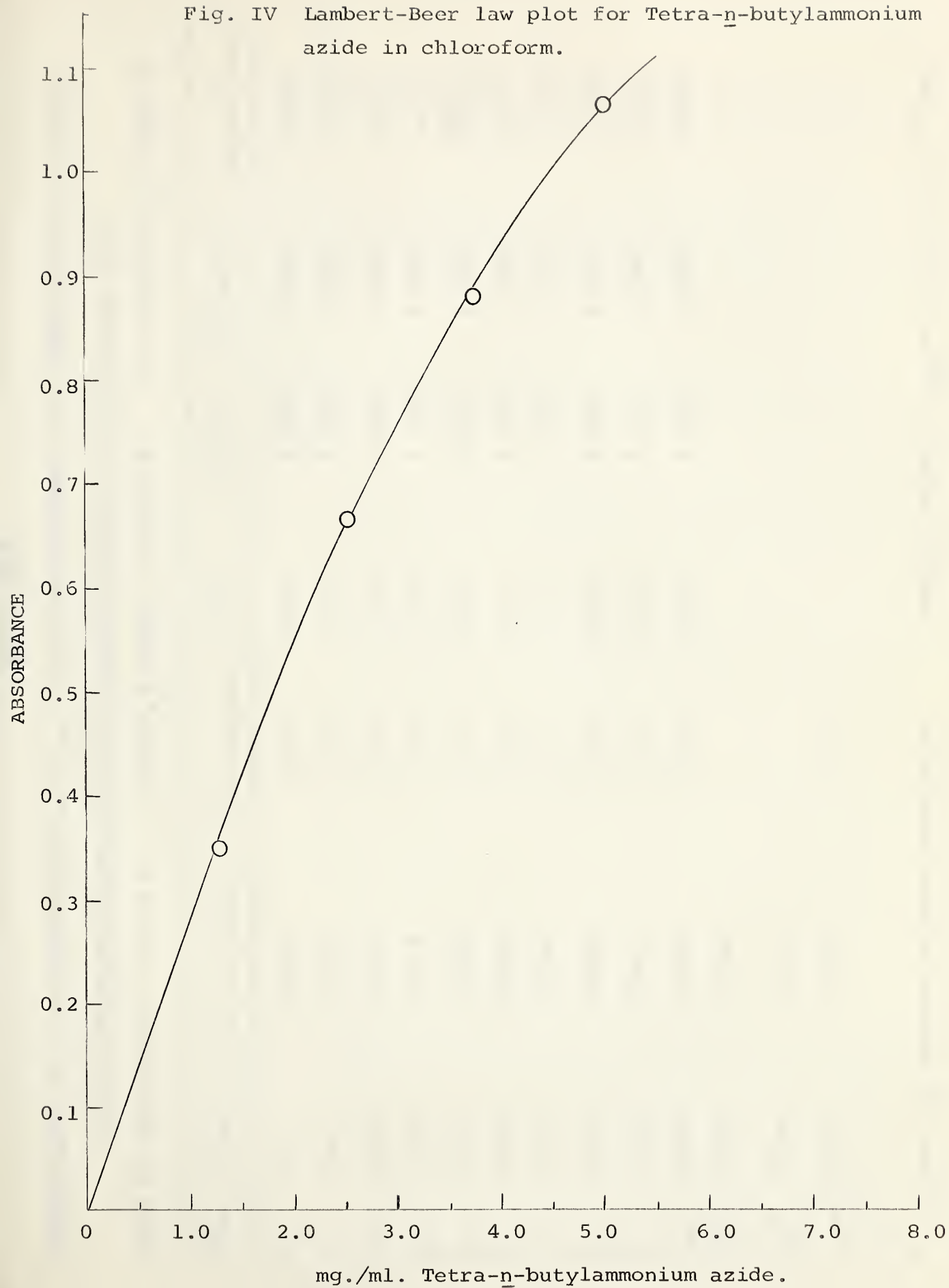


Fig. IV Lambert-Beer law plot for Tetra-n-butylammonium azide in chloroform.



Calculations for the determination of $k_{ob.}$ in the rearrangement and substitution of trityl

2-methylbenzenesulfinate in chloroform with added 2,6-lutidine at 25°C.

Run # 20 [Sulfinate] = 0.025 M.; [(n-Bu)₄N azide] = 0.0256 M.; [2,6-lutidine] = 0.0295 M.

Time	(sec.)	$A_{ob.}(\log I_0/I)$	$A_{ob.}(\text{mg./ml.})$	(a-x)	$\log(a-x)$	$\log(a_0/a-x)$	$k_{ob.} \times 10^4 \text{ sec.}^{-1}$
t_1	375	0.0214	0.07	0.35	1.5441	0.0791	4.85
t_2	740	0.0325	0.15	0.27	1.4314	0.1918	5.95
t_3	1080	0.0391	0.20	0.22	1.3424	0.2808	6.00
t_4	1355	0.0414	0.20	0.22	1.3424	0.2808	4.78
t_5	1625	0.0468	0.23	0.19	1.2788	0.3444	4.87
t_6	1900	0.0505	0.25	0.17	1.2304	0.3928	4.75
t_7	2243	0.0558	0.30	0.12	1.0792	0.5440	5.59
t_8	2834	0.0602	0.32	0.10	1.000	0.6232	5.08
t_9	3510	0.0641	0.35	0.07	2.8451	0.7781	5.10
t_{10}	3835	0.0648	0.35	0.07	2.8451	0.7781	4.69
t_{11}^a	4350	0.3504	-	-	-	-	-
t_{12}^a	8580	0.3527	-	-	-	-	-
$t_{13}=t_\infty$	8910	0.0787	0.42	-	-	-	-

^a t_{11} and t_{12} measure sulfone absorbance Average value of $k_{ob.} = 5.16 \pm 0.40 \times 10^{-4} \text{ sec.}^{-1}$

Table XIII.

Calculations for the determination of $k_{ob.}$ in the rearrangement and substitution of trityl

2-methylbenzenesulfinate in acetonitrile at 25°C.

Run # 36 [Sulfinate] = 0.0260 M.; [(n-Bu)₄N azide] = 0.0260 M.

Time (min.)	$A_{ob}(\log I_0/I)$	$A_{ob}(\text{mg./ml.})$	(a-x)	$\log(a-x)$	$\log(a_0/a-x)$	Let $t_1=t_0$ time and $\log(a_0/a-x)$ become: Time (min.) $\log(a_0/a-x) k_{ob.} \times 10^3 (\text{sec.}^{-1})$	and values for
t_1 6	0.0978	0.575	1.895	0.2777	0.1150	3.5	0.0902 0.99
t_2 $9\frac{1}{2}$	0.1458	0.930	1.54	0.1875	0.2052		
t_3 $12\frac{1}{2}$	0.1877	1.22	1.25	0.0969	0.2958	6.5	0.1808 1.06
t_4 $15\frac{1}{2}$	0.2118	1.40	1.07	0.0294	0.3633	9.5	0.2483 1.00
t_5 18	0.2375	1.60	0.87	1.9395	0.4532	12.0	0.3382 1.08
t_6 22	0.2589	1.76	0.71	1.8513	0.5414	16.0	0.4264 1.02
t_7 24	0.2746	1.90	0.57	1.7559	0.6368	18.0	0.5218 1.11
t_8 27	0.2919	2.02	0.45	1.6532	0.7395	21.0	0.6245 1.14
t_9 30	0.2987	2.07	0.40	1.6021	0.7906	24.0	0.6756 1.08
t_{10} $32\frac{1}{2}$	0.3080	2.15	0.32	1.5051	0.8876	26.5	0.7726 1.12
t_{11} $35\frac{1}{2}$	0.3166	2.22	0.25	1.3979	0.9948	29.5	0.8798 1.14
t_{12} 39	0.3224	2.27	0.20	1.3010	1.0917	33.0	0.9767 1.13
t_{13} $47\frac{1}{2}$	0.3373	2.40	0.07	2.8451	1.5476	41.5	1.4326 1.32
t_{14} 127	0.3454	2.47	-	-	-	-	-

Average value of $k_{ob.} = 1.08 \pm 0.045 \times 10^{-3} \text{ sec.}^{-1}$

DISCUSSION

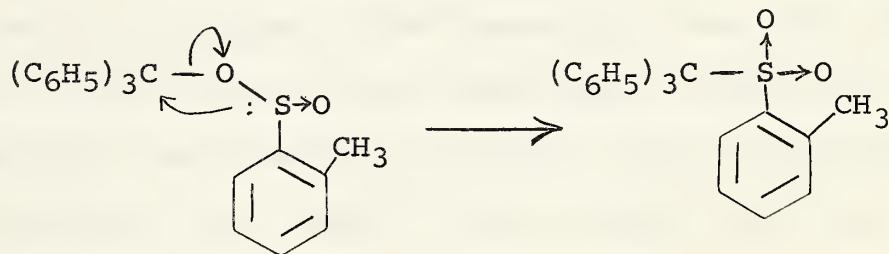
An elucidation of the mechanism of rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone has been based on results from three sources :

- (a) Solvent effects,
- (b) Independent salt exchange studies of trityl perchlorate and sulfinate salts,
- (c) Competition reactions with nucleophiles.

The discussion here will be limited to the results outlined in this chapter for competition reactions with nucleophiles. When necessary, in an interpretation, contributory supporting evidence from solvent effects and salt exchanges will be briefly mentioned, but not fully discussed here. Such discussion and correlation will be given in Chapters III and IV.

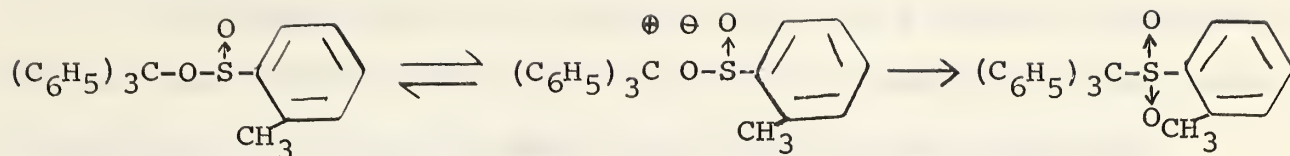
There are two possible mechanisms which can be proposed to explain the rearrangement of the 2-methyl sulfinate to the 2-methyl sulfone.

Mechanism I.



Mechanism I would involve an internal, non-ionic, cyclic rearrangement where the unpaired electrons of sulfur attack the triphenylmethyl carbonyl carbon, concerted with migration of the bonding carbon-oxygen electrons to the oxygen. The net result is carbon-sulfur bond formation without the development of an ionic transition state.

Mechanism II.



In Mechanism II, the rearrangement would occur by ionization, with the generation and subsequent recombination of ion pairs to give the rearranged product.

Mechanism II explains the appearance of trityl azide as the substitution product, and indicates the existence of a capturable carbonium ion intermediate in the reaction scheme. This by no means excludes Mechanism I to explain the production of some sulfone, since both mechanisms could be concurrently operative. An analysis of the kinetic data merits presentation at this stage.

We have seen that the rearrangement of the 2-methyl ester to the corresponding sulfone in the absence of azide ion is first order in ester. Calculated first order rate constants for the formation of trityl azide were found to vary by a factor of 28 (24.2 to 685) over a sixteenfold concentration range of ionic azide, while calculated second order rate constants changed by a factor of 2 (1.81 to 3.32) over this range (Table VIII). This indicates that the formation of trityl azide is an overall second-order process, first order in ionic azide, and first order in ester.

In the presence of azide ion, the observed rate of ester disappearance was found to increase by a factor of 2.5 over a sixteenfold concentration range of ionic azide. In interpreting this observation, the possibility of a direct displacement reaction occurring on the ester by the azide ion should be considered.

Evidence which was found to rule out a direct displacement reaction was obtained from the results of a comparison of the rates of exchange of tetra-n-butylammonium azide and tetra-n-butylammonium 2-methylbenzenesulfinate with the 2,6-dimethyl ester. Equimolar amounts (0.025 M.) of ester and sulfinate salt produced the same quantity of sulfone in 1350 min. that was produced in the rearrangement of the 2-methyl ester in 6 min. A comparison of the times required to produce the same amount of sulfone from the same concentrations of the two esters is indicative of the relative rates of formation of sulfone from the esters. Thus:

$$\frac{k_{\text{rearrg.}}}{k_{\text{exch.}}} = \frac{1350}{6} = 225$$

$$\text{but } k_{\text{rearrg.}} = 5.57 \times 10^{-4} \text{ (Table IV)}$$

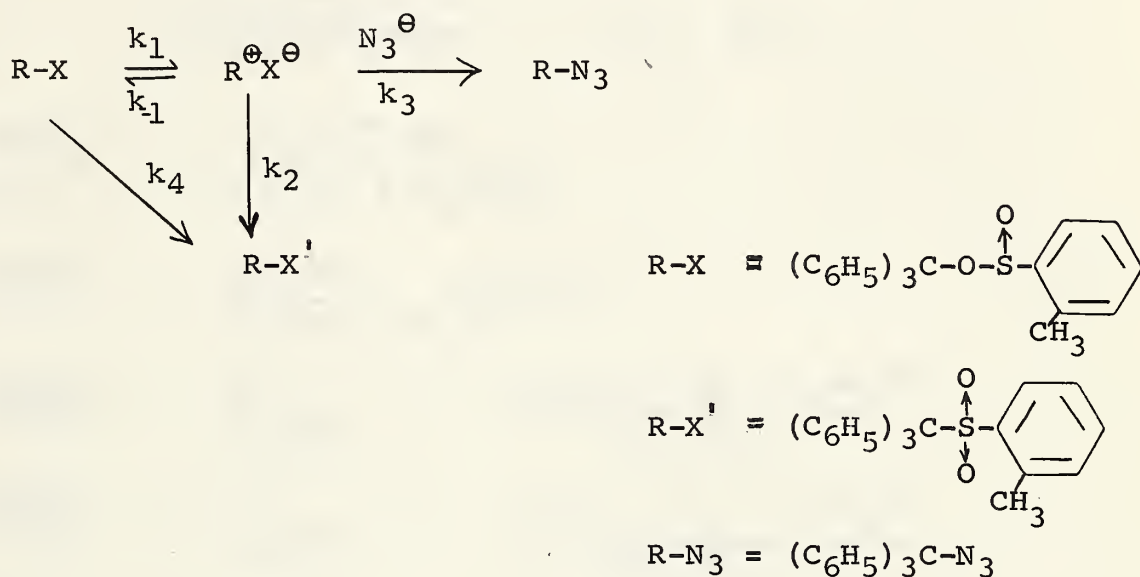
$$\therefore k_{\text{exch.}} = 2.5 \times 10^{-6} \text{ sec.}^{-1}$$

which gives a measure of the pseudo-first-order rate for the exchange reaction. From Table IX, $k_{\text{ob.}} = 7.55 \times 10^{-6} \text{ sec.}^{-1}$ at approximately the same concentrations of 2,6-dimethyl ester and ionic azide. These values would not be expected to agree within a factor or three if a direct displacement were operative here.

The results from the competition experiments therefore suggest an ionization process in operation, rather than a direct displacement reaction.

Before setting up a reaction scheme to explain these results, it should be pointed out that on examination of Table VIII, it may be seen that at a constant concentration of 2-methyl ester, the percentage of trityl azide produced increases and the percentage of 2-methyl sulfone is reduced, when the concentration of ionic

azide is increased relative to ester. Since this is not a direct displacement reaction, the observed reduced yields of sulfone on increasing the mole ratio of ionic azide, suggests that both products arise from a common ion pair intermediate. A reaction scheme may be set up as in the following :



This scheme takes into account the production of sulfone from any other source besides that of a common trapable ion pair intermediate for trityl azide and sulfone production, and is accounted for by k_4 . This includes sulfone produced in the cyclic, non-ionic process, and by way of ionic species which are not common capturable ionic species for trityl azide and sulfone formation. A complete kinetic expression may be derived in order to determine the fraction of sulfone produced from a common trappable ion pair intermediate in the concurrent rearrangement and substitution:

$$\begin{aligned}
 \frac{-d[\text{RX}]}{dt} &= (k_1 + k_4) [\text{RX}] - k_{-1} [\text{R}^{\oplus}\text{X}^{\ominus}] \\
 \frac{+d[\text{RX}^{\oplus\ominus}]}{dt} &= k_1 [\text{RX}] - k_{-1} [\text{R}^{\oplus}\text{X}^{\ominus}] - k_2 [\text{R}^{\oplus}\text{X}^{\ominus}] - k_3 [\text{R}^{\oplus}\text{X}^{\ominus}] [\text{N}_3^{\ominus}]
 \end{aligned}$$

Assuming the steady state approximation, then:

$$[R^{\oplus}X^{\ominus}] = \frac{k_1 [R-X]}{k_{-1} + k_2 + k_3 [N_3^{\ominus}]}$$

whence

$$\begin{aligned} \frac{-d[RX]}{dt} &= k_1 [RX] + k_4 [RX] - \frac{k_{-1}k_1 [RX]}{k_{-1} + k_2 + k_3 [N_3^{\ominus}]} \\ &= \left\{ \frac{k_1 (k_2 + k_3 [N_3^{\ominus}])}{k_{-1} + k_2 + k_3 [N_3^{\ominus}]} + k_4 \right\} [RX] \end{aligned}$$

$$\frac{d[RN_3]}{dt} = \frac{k_1 k_3 [N_3^{\ominus}] [RX]}{k_{-1} + k_2 + k_3 [N_3^{\ominus}]}$$

$$\frac{d[RX']}{dt} = \frac{k_1 k_2 [RX]}{k_{-1} + k_2 + k_3 [N_3^{\ominus}]} + k_4 [RX]$$

$$\frac{d[RX']}{d[RN_3]} = \frac{k_2}{k_3 [N_3^{\ominus}]} + \frac{k_4 (k_{-1} + k_2 + k_3 [N_3^{\ominus}])}{k_1 k_3 [N_3^{\ominus}]}$$

$$\frac{[RX']}{[RN_3]} = \frac{k_2}{k_3 [N_3^{\ominus}]} + \frac{k_4 (k_{-1} + k_2 + k_3 [N_3^{\ominus}])}{k_1 k_3 [N_3^{\ominus}]}$$

Let $F_{\text{azide}} = \frac{[RN_3]}{[RN_3] + [RX']} = \text{fraction of RX producing } RN_3$

then $\frac{1}{F_{\text{azide}}} = \frac{[RX']}{[RN_3]} + 1 = \frac{[RX'] + [RN_3]}{[RN_3]} = \frac{k_2 + k_3 [N_3^{\ominus}]}{k_3 [N_3^{\ominus}]} + \frac{k_4 (k_{-1} + k_2 + k_3 [N_3^{\ominus}])}{k_1 k_3 [N_3^{\ominus}]}$

$$= \frac{(k_1 + k_4) (k_2 + k_3 [N_3^{\ominus}]) + k_{-1} k_4}{k_1 k_3 [N_3^{\ominus}]}$$

Let $k_4 = Rk_1$

then $\frac{1}{F_{\text{azide}}} = \frac{(R+1) (k_2 + k_3 [N_3^{\ominus}]) + k_{-1} R}{k_3 [N_3^{\ominus}]}$

$$= \frac{R(k_{-1} + k_2) + k_2}{k_3 [N_3^{\ominus}]} + (R+1)$$

A plot of $\frac{1}{F_{\text{azide}}} \text{ vs. } \frac{1}{[N_3^{\ominus}]}$ will yield a straight line with slope

$$= \frac{R(k_{-1} + k_2)}{k_3} \quad \text{and Intercept} = (R+1)$$

From the intercept a value of R can be obtained. Such a plot is given in Fig. V. From Fig. V, Intercept = (R + 1) = 1

$$\therefore R = 0$$

$$\therefore k_4 = 0$$

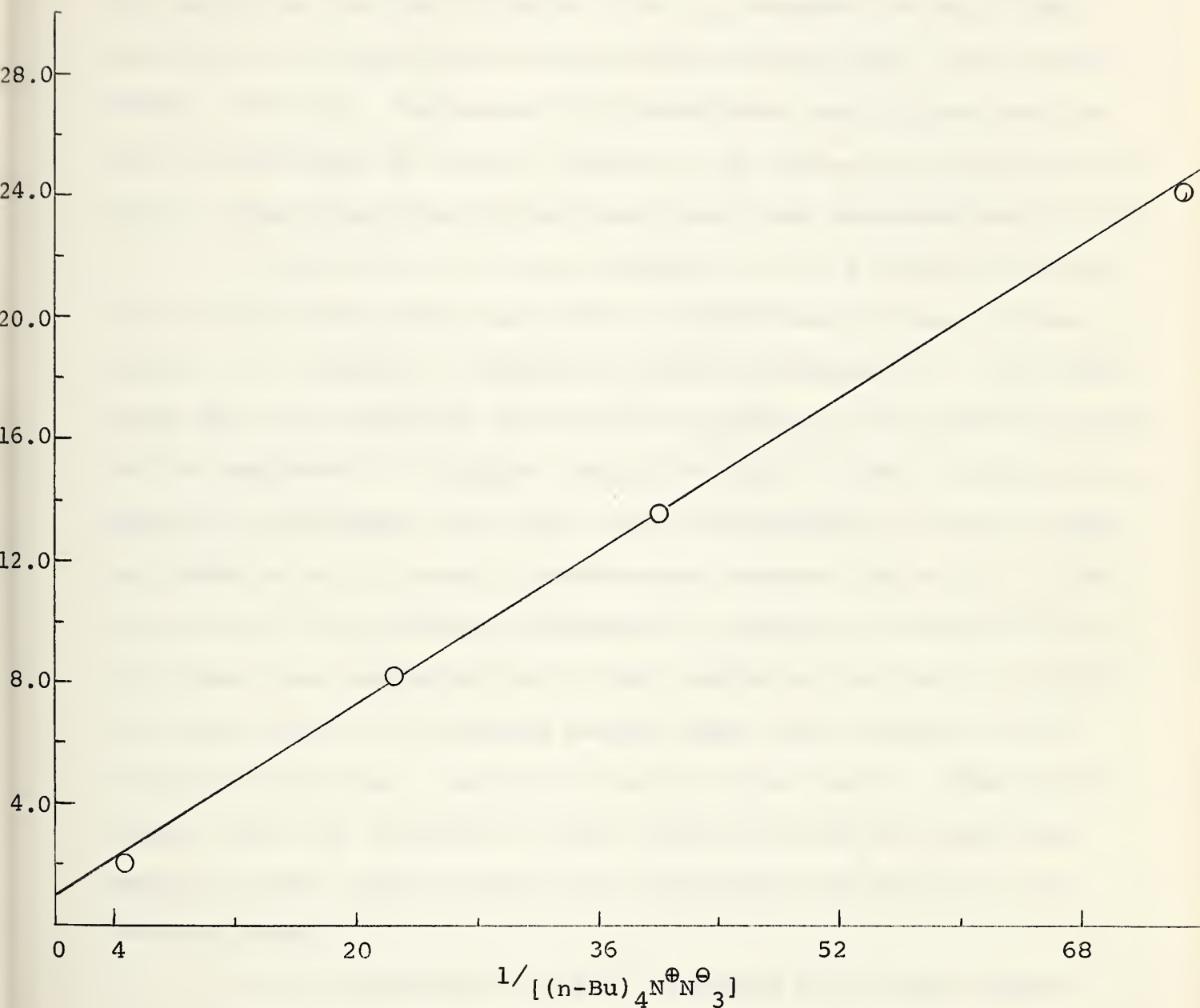


Fig. V. Plot of the reciprocal of the concentration of ionic azide versus the reciprocal of the fraction of trityl azide in the concurrent rearrangement and substitution of the 2-methyl ester, to show that the greatest fraction of sulfone is produced by an ionization pathway.

These results therefore suggest, that at least the greatest fraction, if not all of the rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone proceeds by way of Mechanism II, the ionization mechanism, rather than by Mechanism I. The nature of the ionic species, that is, whether the capturable species is an intimate or solvent separated ion pair, (54) is not known. However, the absence of dissociated ions is precluded by use of chloroform as solvent, since in low dielectric solvents, ion pairs, rather than dissociated ions, have been characterized (15,25).

The results from the reactions of the 2,6-dimethyl ester and the quaternary ammonium azide in chloroform provide evidence to support the validity of Mechanism II over Mechanism I. Since this ester does not rearrange to sulfone, analysis of the mechanism could not be conducted in a manner similar to that for the 2-methyl ester. However, in exchange with azide ion, the formation of trityl azide was found to be an overall second-order process (Table IX). The first-order rate constant increased by a factor of eleven (7.55 to 83.6) when the concentration of ionic azide was varied by a factor of seven, but, the calculated second order rate constant did not change by more than a factor of two over this range. This would suggest that the reaction is first order in azide ion, and first order in ester, which results are consistent with those for the 2-methyl ester.

It is noteworthy to draw attention to the high concentration of ionic azide which was required to trap 46% of the carbonium ion. Despite the powerful nucleophilicity of the azide ion, and the high concentration used relative to ester, all of the carbonium ion was not trapped, indicating that collapse of the ion pair to

give sulfone is very much faster than exchange with the azide ion. Support for this interpretation is provided from the results in Chapter IV. With poorer nucleophiles such as ethanol, no trapping occurred, or if trapping occurred, the amount of trapped product was undetectable. Also in Chapter IV, evidence is provided to show that k_{-1} in the reaction scheme for the 2-methyl ester, is negligible compared to k_2 . This means that no ion-pair return occurs to regenerate this ester in chloroform. However, in the 2,6-dimethyl ester, k_{-1} becomes very important relative to $k_3[N_3^\ominus]$ because the value of k_2 (relative to the 2-methyl ester) has diminished considerably since no sulfone is produced from this ester.

Increased rates of exchange and rearrangement have been observed in solvents of higher ionizing power. The criterion that ionization reactions proceed more rapidly in solvents of higher ionizing power than in solvents of low ionizing power holds here. This will be dealt with in Chapter III.

The exceedingly fast rate of rearrangement observed in the absence of a base was mentioned earlier. The reaction proceeds more slowly in the presence of azide ion or 2,6-lutidine. The latter base reacts with the trityl cation, but the reaction product could apparently exchange with more powerful nucleophiles when they are present in the same reaction mixture (Chapter IV). If one considers azide anion cannot trap more than 3% of the trityl cation when equimolar amounts of ester and nucleophile are present, it would be highly unlikely that the exchange occurring in these concurrent substitutions and rearrangements is one involving trityl lutidinium salts especially when we compare the relative nucleophilicity of the azide ion and 2,6-lutidine (39).

Compared to carbon disulfide and carbon tetrachloride, whose dielectric constants at 20°C. are 2.64 and 2.22 respectively, chloroform (of dielectric constant 4.80 at 20°C.) is a much better ionizing solvent for these esters, despite its low dielectric constant. Perhaps the strongly acidic hydrogen in the molecule hydrogen bonds with the ester, and thus assists in ionization.

In concluding this discussion, attention should be directed to the direct comparison of the rates of ionization of the 2-methyl, 4-methyl and 2,6-dimethyl esters in chloroform, which is available from these data. In Table IV, a comparison of Runs 10 and 11 shows the 4-methyl ester to be approximately twice as fast as the 2-methyl ester. Comparing Runs 21 and 24 with Runs 31 and 42, shows the 2-methyl ester to be 6-8 times faster in exchange than the 2,6-dimethyl ester. To the extent that the amount of ion pair return is the same in both systems, then this is a comparative measure of ionization for both esters.

EXPERIMENTAL

Reagents

Tetra-n-butylammonium bromide was prepared by use of the method of Darwish (55). Starting with equimolar quantities of tri-n-butyl amine and n-butyl bromide, a 48.5% yield of product was obtained. Four recrystallizations from ethyl acetate yielded a white crystalline product m.p. 119-121°C.

Tetra-n-butylammonium 2-methylbenzenesulfinate was prepared by the neutralization of tetra-n-butylammonium hydroxide with 2-methylbenzenesulfinic acid. To 30 g. (0.0932 mole) of tetra-n-butylammonium bromide in 35 ml. of water was added 0.0466 mole (10.8 g.) of silver oxide, and the mixture stirred until a negative test for bromide ion was obtained, indicating complete consumption of the bromide. The solution was filtered through a sintered-glass funnel, and the silver bromide precipitate washed with several portions of water. To the filtrate, the solid sulfinic acid was added gradually, with stirring, until the solution was neutral to litmus. Approximately 16 g. of acid were required.

The resulting neutral solution was then evaporated in an evaporating dish on a hot plate, with a stream of air passing over the solution to remove excess water, making sure that the temperature did not rise over 70°C. On the first appearance of crystals, the yellow oil was transferred to a dessicator, and dried by pumping under a vacuum over phosphorus pentoxide as dessicant using an oil pump, to ensure complete removal of water. The yellow solid obtained was found to be hygroscopic.

Weight product = 19 g.; Yield = 51.5% based on weight of starting bromide. Recrystallization from ethyl acetate yielded white crystals

of m.p. 101-102°C. N.M.R. data: The methylene protons of the n-butyl groups adjacent to nitrogen appear as a complex multiplet at 6.7-7.15 τ , while the rest of the methylene and methyl protons of the butyl groups appear from 8.1-9.3 τ also as a complex multiplet. Respectively, the calculated ratio for these protons is 1:3.5. The found integrated ratio was 1:3.6. The sulfinate aromatic protons show a complex multiplet at 2.5 to 2.85 τ and a quartet at 2.25 τ assigned to the hydrogen ortho to the carbon adjacent to sulfur. The calculated ratio of 1:3 for this proton and other aromatic protons agrees with the found ratio of 1:3. The found ratio of 1:9.77 of aromatic to all other protons agrees with the calculated ratio of 1:9.8. A singlet at 7.3 τ was indicative of the methyl protons. The found integrated ratio of 1:12.8 for methyl to all other protons agreed fairly well with calculated of 1:13.3. These spectra were run in deuterated water. I.R. data: Strongly absorbing bands at 970 and 1050 cm^{-1} , in addition to the aromatic substitution bands at 720, 740, 870 cm^{-1} in Nujol.

Tetra-n-butylammonium 2,6-dimethylbenzenesulfinate was prepared by the method described for the 2-methyl salt. Starting with 30 g. (0.0913 mole) of tetra-n-butylammonium bromide, and 12 g. of silver oxide, after isolation, 15.6 g. (0.0376 mole) of crude product was obtained melting at 58-64°C. and corresponding to a 38.6% yield. Three recrystallizations from ethyl acetate yielded salt of m.p. 90-91°C. N.M.R. data: A singlet for the methyl protons was observed at 7.36 τ and a complex multiplet at 2.0-2.8 τ for the aromatic protons. The found integrated ratio of 3.22:1 for methyl to aromatic protons does not agree with the calculated ratio of 2:1. The proton signals and integrated ratios for the n-butyl group are the same as reported for the 2-methyl salt.

I.R. data: The intense bands observed here were similar to those observed for the 2-methyl salt at 720, 740, 870, 970 and 1050 cm^{-1} . Tetra-n-butylammonium azide was prepared as previously described (25) by the neutralization of the hydroxide with hydrazoic acid, followed by several recrystallizations from benzene. The characteristic band at 2110 cm^{-1} was found in the I.R., and the N.M.R. showed the usual complex for the tetra-n-butyl grouping in the region 6.5, 7.5 and 9.0 τ as described for the 2-methylsulfinate salt. In view of its extremely hygroscopic nature, this compound has to be stored in a dessicator over phosphorus pentoxide under vacuum. Use of the compound was accomplished by means of insertion of a length of glass tubing into the solid sample, allowing the solid to rise up the tubing, followed by a quick transferal of the tubing (with sample) into a tared container, and subsequent ejection of the sample by means of a length of glass rod.

Trityl azide was prepared by the reaction of trityl isothiocyanate with sodium azide in acetone-water (15).

(a) Trityl isothiocyanate was synthesized by the procedure suggested by Mazzuccato (56). A solution of 27.8 g. (0.0965 mole) of trityl chloride in 100 ml. acetone was added to 12 g. (0.123 mole) potassium thiocyanate (Fisher reagent grade) and allowed to sit at room temperature for 4 hrs. After this period of time the mixture was filtered, and the solvent evaporated under an aspirator to a volume of 80 ml., after which precipitation of the product was effected by cooling the reaction mixture to 0°C. The weight of crude product obtained was 24.6 g. (0.065 mole) of m.p. 133-135°C. (reported m.p. 136-138 cm^{-1} (56)), and corresponded to a 67.5% yield.

(b) Trityl Azide Fisher reagent grade sodium azide (8.15 g.;

0.125 mole) was dissolved in 650 ml. of water, and this solution was added to a solution of 12.5 g. (0.0415 mole) of trityl isothiocyanate in 1000 ml. of acetone. After 24 hrs. at room temperature, 1250 ml. of water was added, and the solution extracted thrice with ether and once with benzene. The combined extracts were dried over anhydrous magnesium sulfate, and the solvents removed by evaporation under an aspirator, assisted by warming of the filter flask with an 80° water bath. The crude product was recrystallized three times from acetone-water to yield 8.7 g. of trityl azide of m.p. 62-64°C. (reported m.p. 64.5-65.5°C. (15)). This corresponded to a 70% yield.

I.R. data: In carbon disulfide intense bands were observed at 700, 750, 1250 and 2100 cm^{-1} .

Procedures

Kinetic Measurements

(a) Rate Runs for the Rearrangement of Sulfinates to Sulfones

A sample of ester was accurately weighed on a watchglass, and then transferred to a 10 ml. volumetric flask with a nichrome spatula. Traces of ester remaining on the watchglass and spatula were washed into the flask with aliquots of solvent, followed by addition of more solvent to bring the volume up to the mark. The ester was dissolved by shaking the flask. On addition of the first aliquot of solvent to the ester the time was recorded.

An aliquot of the reaction mixture was then removed by a hypodermic syringe and transferred to a 0.5 mm. cell which had been previously matched with a variable spacer type cell in order to reduce the absorbance by the solvent to a minimum (by compensation) in the region to be scanned. Using a Perkin Elmer 21 Infrared

Spectrophotometer, with a 20 cm. per micron scale setting, the region of 7.3 to 8.1 microns was scanned at room temperature (25-26°C.) at a slit opening of 0.68 millimicrons to determine the absorbance of the sulfone band at 7.73 microns. The time recorded for a particular point in a run was that at which the apex of the sulfone peak was reached at 7.73 microns. After a point had been taken, the instrument was immediately reversed to the starting scale reading (7.3 microns), and the range was rescanned.

(b) Rate Runs for the Concurrent Rearrangement and Substitution

For runs in which the sulfone band is followed, the procedure used is the same as that described in part (a) for the rearrangement of the sulfinate to the sulfone. After the maximum amount of sulfone had been produced, trityl azide absorbance at 4.79 microns and tetra-*n*-butyl-ammonium azide absorbance at 5.01 microns was determined by scanning the range 4.55 to 5.4 microns.

(c) Rate Runs which follow the Trityl Azide Band

The detailed procedure described for measuring the sulfone absorbance applies here also. Absorbance for the trityl azide band at 4.79 microns was determined by scanning the range 4.55 to 5.4 microns.

Lambert-Beer Law determinations

Trityl Azide in Chloroform, Acetonitrile and Dimethylsulfoxide

For each determination a standard solution of trityl azide was prepared by transferring 0.8111 g. (0.00296 mole) of the compound into a 100 ml. volumetric flask followed by addition of the solvent up to the mark to give a 0.0296 M. solution. In order to obtain 20, 40, 60 and 80% solutions, one, two, three and four 5 ml. aliquots of standard solution were removed and transferred to 25 ml. volumetric

flasks using the same automatic 5 ml. pipette, followed by addition of the solvent to the mark to obtain the required concentration.

Samples of these solutions were scanned in the region of 4.4 to 5.15 microns on a Perkin Elmer 21 instrument at a 20 cm. per micron scale setting in order to determine the absorbance values.

Tetra-n-butylammonium Azide in Chloroform

A 0.0218 M. solution of the azide in chloroform containing 0.0302 M. 2,6-lutidine, was used for the determination. The procedure is similar to that described below for trityl azide and the region 4.5 to 5.35 microns was scanned.

Trityl 2-Methylphenyl Sulfone

A 0.030 M. solution of sulfone in chloroform was obtained by dissolving 1.1934 g. (0.003 mole) of trityl 2-methylbenzenesulfinate in chloroform and allowing the solution to sit at room temperature for $5\frac{1}{2}$ hrs. The procedure used thereafter is similar to that described for trityl azide. The region 7.3 to 8.3 microns was scanned to determine the absorbance of the solutions.

Reaction Products

Trityl azide and trityl 2-methylphenyl sulfone were identified by their I.R. spectra, which were found to be identical to spectra of authentic samples of these compounds which have been previously described here and in Chapter 1.

CHAPTER III

Rearrangement and Substitution Processes in Solvents of High

Dielectric Constant

After it was established that a common, capturable ion pair intermediate existed for the production of trityl 2-methylphenyl sulfone and trityl azide in the concurrent rearrangement and substitution of trityl 2-methylbenzenesulfinate in chloroform, our interest then extended to studies of these reactions in solvents of higher dielectric constant. The objective of these investigations was to determine if the same common trappable ionic species shown to be present in chloroform, also existed in these solvents. Furthermore, it was believed that if the rearrangement of sulfinate to sulfone did proceed by way of ionization rather than an internal, cyclic, non-ionic process, then these substrate systems would be sensitive to solvent effects.

RESULTS

The selection of a high dielectric constant solvent for these studies was limited by the reactivity of the solvent towards the substrate, and also to the absorption of the solvent in the I.R. and N.M.R., relative to that of the 2-methyl sulfone. Of the common non-hydroxylic solvents of high dielectric constant (acetonitrile, nitromethane, dimethylformamide, acetone, dimethylsulfoxide and nitrobenzene), none were suitable for use in the I.R. to follow the appearance of the sulfone band, since they all absorbed strongly in the region of 7.3 to 7.9 microns. In the N.M.R., nitrobenzene was the only one suitable for this purpose, since there was no interference in the region where the methyl protons gave signals

for both the ester and the sulfone.

The half-life for the first-order rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone, in nitrobenzene at room temperature in the N.M.R. was found to be approximately nine minutes. The data is presented in Table XIV.

Table XIV.

The rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone in nitrobenzene at 25°C.^a

Trityl 2-methyl	τ value for $-\text{CH}_3$ protons	Reaction time (min.)	Integrated ratio	Mole % at time t	Mole % corrected ^b
sulfinate (0.100 M)	8.35	9	1:1.7	37	49.3
		46	0	0	0
sulfone	8.72	9	1.7:1	63	50.7
		46	∞	100	100

^a 0.021 M in 2,6-lutidine with tetramethyl silane as external standard

^b 75% pure in ester

Since the sample of ester used contains 25% sulfone, a correction for the percentage of sulfone produced in the rearrangement has to be made, and the calculation for the half-life period was done in the following manner:

From the integrated values,

At time = 9 min.

$$\frac{[\text{Ester}]}{[\text{Sulfone}]} = \frac{1.5}{2.5} = \frac{1}{1.7}$$

or

$$\% \text{ Ester} = \frac{1}{2.7} \times 100 = 37\%$$

$$\% \text{ Sulfone} = 100 - 37 = 63\%$$

From an N.M.R. spectrum of the sulfinat in carbon disulfide, the ester was found to be 75% pure since the integrated ratio:

$$\frac{[\text{Ester}]}{[\text{Sulfone}]} = \frac{3}{1}$$

$$\therefore \text{Sulfone produced during run} = 63 - 25 = 38\%$$

$$\therefore \text{Corrected \% Sulfone} = \frac{38}{75} \times 100 = 50.7\%$$

$$\text{Corrected \% Ester} = 100 - 50.7 = 49.3\%$$

From this data, this means that the compound has a half-life of approximately 9 min. in nitrobenzene with added 2,6-lutidine at 25°C.

Since it was not possible to follow sulfone appearance in the I.R. using the aforementioned solvents, the rate of formation of trityl azide was followed in substitution reactions of tetra-*n*-butylammonium azide with the 2-methyl sulfinat, because these solvents do not absorb in the region where the azide band appears (4.79 microns). Under similar conditions, it was also possible to determine the rate of trityl azide production from the exchange of the 2,6-dimethyl sulfinat and ionic azide.

The exchange of tetra-*n*-butylammonium azide with equimolar amounts of trityl 2,6-dimethylbenzenesulfinat, in acetonitrile, was found to be an overall first-order process, with an observed rate constant of $8.55 \pm 0.536 \times 10^{-5} \text{ sec.}^{-1}$. A downward drift in rate was discernible (Table XV). When the concentration of ionic azide was varied from 0.02 to 0.26 M, at a constant concentration of ester (0.023 M.) the reaction rate only increased by a factor of two, which increase could be due to a salt effect, (see Table XVI). This indicates a first, and not a second-order process, to be operative

Table XV.

Calculations for the determination of $k_{ob.}$ in the substitution of Trityl 2,6-dimethylbenzene-sulfinate with tetra-n-butylammonium azide at equimolar concentration, in acetonitrile at 25°C.

Run # 35 [Sulfinate] = 0.0288 M. [Azide] = 0.0286 M.

Time (min.)	$A_{ob.}$	$(\log I_0/I)$	$A_{ob.}$ (mg./ml)	(a-x)	$\log(a-x)$	$\log(a_0/a-x)$	$k_{ob.} \times 10^5$ (sec. ⁻¹)
t_1	5	0.0328	0.15	6.35		0.0101	
t_2	13	0.0654	0.35	6.15	0.8028	0.0240	
t_3	18	0.0887	0.50	6.00	0.7889	0.0347	
t_4	22	0.1083	0.65	5.85	0.7782	0.0457	
t_5	27	0.1262	0.77	5.73	0.7672	0.0547	
t_6	32	0.1495	0.95	5.55	0.7582	0.0686	
t_7	36	0.1701	1.10	5.40	0.7443	0.0805	
t_8	41	0.1918	1.25	5.25	0.7324	0.0927	
t_9	45	0.2054	1.35	5.15	0.7202	0.1011	
t_{10}	51	0.2214	1.52	4.98	0.7118	0.1157	
t_{11}	56	0.2458	1.67	4.83	0.6972	0.1290	
t_{12}	61 $\frac{1}{2}$	0.2728	1.87	4.63	0.6839	0.1473	
t_{13}	67	0.2768	1.93	4.57	0.6656	0.1530	
t_{14}	71	0.294	2.05	4.45	0.6599	0.1645	
t_{15}	78	0.3127	2.20	4.30	0.6484	0.1794	
t_{16}	84 $\frac{1}{2}$	0.3258	2.30	4.20	0.6335	0.1897	

let $t_7 = t_0$ then

$\log(a_0/a-x)$ and Time and k_{ob}

becomes

becomes

0.0122 5 9.35

0.0206 9 8.80

0.0352 15 8.97

0.0485 20 9.30

0.0668 25 $\frac{1}{2}$ 10.20

0.0725 31 8.95

0.0838 35 9.20

0.0987 42 9.00

0.1092 48 $\frac{1}{2}$ 8.65

t_{17}	91	0.3435	2.45	4.05	0.6232	0.2054	0.1249	55	8.72
t_{18}	99	0.3735	2.70	3.80	0.6075	0.2331	0.1526	63	9.26
t_{19}	111	0.3922	2.85	3.65	0.5798	0.2506	0.1701	75	8.70
t_{20}	140	0.4448	3.30	3.20	0.5623	0.3078	0.2273	104	8.38
t_{21}	154	0.4603	3.425	3.075	0.5051	0.3251	0.2446	118	7.95
t_{22}	169	0.4875	3.65	2.85	0.4877	0.3581	0.2776	133	7.95
t_{23}	$183\frac{1}{2}$	0.5038	3.775	2.725	0.4548	0.3775	0.2970	$147\frac{1}{2}$	7.76
t_{24}	204	0.5299	4.00	2.50	0.4354	0.4150	0.3345	168	7.65
t_{25}	257	0.5733	4.40	2.10	0.3979	0.4907	0.4102	221	7.13
t_{26}	317	0.6070	4.72	1.78	0.3222	0.5625	0.4820	281	6.58
$t_{27}^{\text{=t}}$	$23\frac{1}{2}\text{hrs.}$	0.7586	6.50	-	-	-	-	-	-

Average value of $k_{\text{ob.}} = 8.55 \pm 0.536 \times 10^{-5} \text{ sec.}^{-1}$

Table XVI.

The Substitution of Trityl 2,6-dimethylbenzenesulfinate with tetra-n-butylammonium azide
in acetonitrile and dimethylsulfoxide at 25°C.

Run	Ester (M)	(n-Bu) ₄ azide (M.)	Solvent	k _{ob.} x 10 ⁵ sec. ⁻¹
35	0.0288	0.0286	Acetonitrile	8.55 ± 0.536
40	0.0290	0.0570	"	9.76 ± 0.397
47	0.0287	0.260	"	14.4 ± 0.058
45	0.0243	0.0243	Dimethylsulfoxide	7.57 ± 0.440

here. At equimolar concentrations, in dimethylsulfoxide as solvent, a first order rate constant of $7.57 \pm 0.44 \times 10^{-5} \text{ sec.}^{-1}$ was obtained (see Table XVI).

The deviation from the Lambert-Beer law for trityl azide in acetonitrile, was found to be the same as that in chloroform (Fig. VI). However, in dimethylsulfoxide, trityl azide absorbance changes very little over a wide concentration range, and the deviation from the Lambert-Beer law is considerably more marked than in acetonitrile and chloroform (see Fig VII).

At equimolar concentrations of ionic azide and 2-methyl ester, rearrangement and substitution proceeds with a first-order rate constant of $1.08 \pm 0.045 \times 10^{-3} \text{ sec.}^{-1}$ in acetonitrile. When the concentration of tetra-n-butylammonium azide was varied relative to ester, which concentration was held constant, there was no change in the rate. The percentage of trityl azide produced during the rearrangement was found to vary between 29.5 and 42.5% over a twenty-fold concentration range of ionic azide. These data are summarized in Table XVII. The difference of 29.5 and 42.5% may be significant in that the amount of carbonium ion trapped depends on the concentration of the nucleophile. However, in Runs 36 to 39, where the concentration range of ionic azide was varied from 0.026 to 0.230 M., the percentage of trityl azide produced remained fairly constant at an average value of 37%. The variation in this value maybe within experimental error.

In dimethylsulfoxide, 23.8 and 29.5% trityl azide were produced in the concurrent rearrangement and exchange on increasing the ionic azide concentration threefold (0.028 to 0.095 M.) relative to ester (0.026 M.). The k_{ob} was found to be $1.11 \pm 0.16 \times 10^{-3} \text{ sec.}^{-1}$ at equimolar concentrations of 2-methyl ester and ionic azide

(see Table XVII).

Table XVII.

The Substitution of Trityl 2-methylbenzenesulfinate with tetra-n-butylammonium azide in acetonitrile and dimethylsulfoxide at 25°C.

Run	Ester (M)	(n-Bu) ₄ N ⁺ azide (M.)	Solvent	% Trityl ^a azide	% Sulfone ^b	k _{ob.} x 10 ³ sec. ⁻¹
38	0.0260	0.0104	Aceto- nitrile	29.5	70.5	1.58 ± 0.048
36	0.0260	0.0260	" "	36.0	64.0	1.08 ± 0.045
37	0.0260	0.0510	" "	35.8	64.2	1.62 ± 0.087
39	0.0260	0.0547	" "	39.4	60.6	Product run
41	0.0264	0.230	" "	42.5	57.5	1.49 ± 0.120
43	0.0260	0.0288	Dimethyl- sulfoxide	23.8	76.2	1.11 ± 0.160
44	0.0252	0.0950	" "	29.5	70.5	5.51 ± 0.300

^a Based on 92.5% pure ester.

^b Obtained by difference.

Trityl 2-methylphenyl sulfone was detected and isolated in these runs in acetonitrile and dimethylfoxide.

Fig. VI. Lambert-Beer law plot for Trityl azide
in acetonitrile

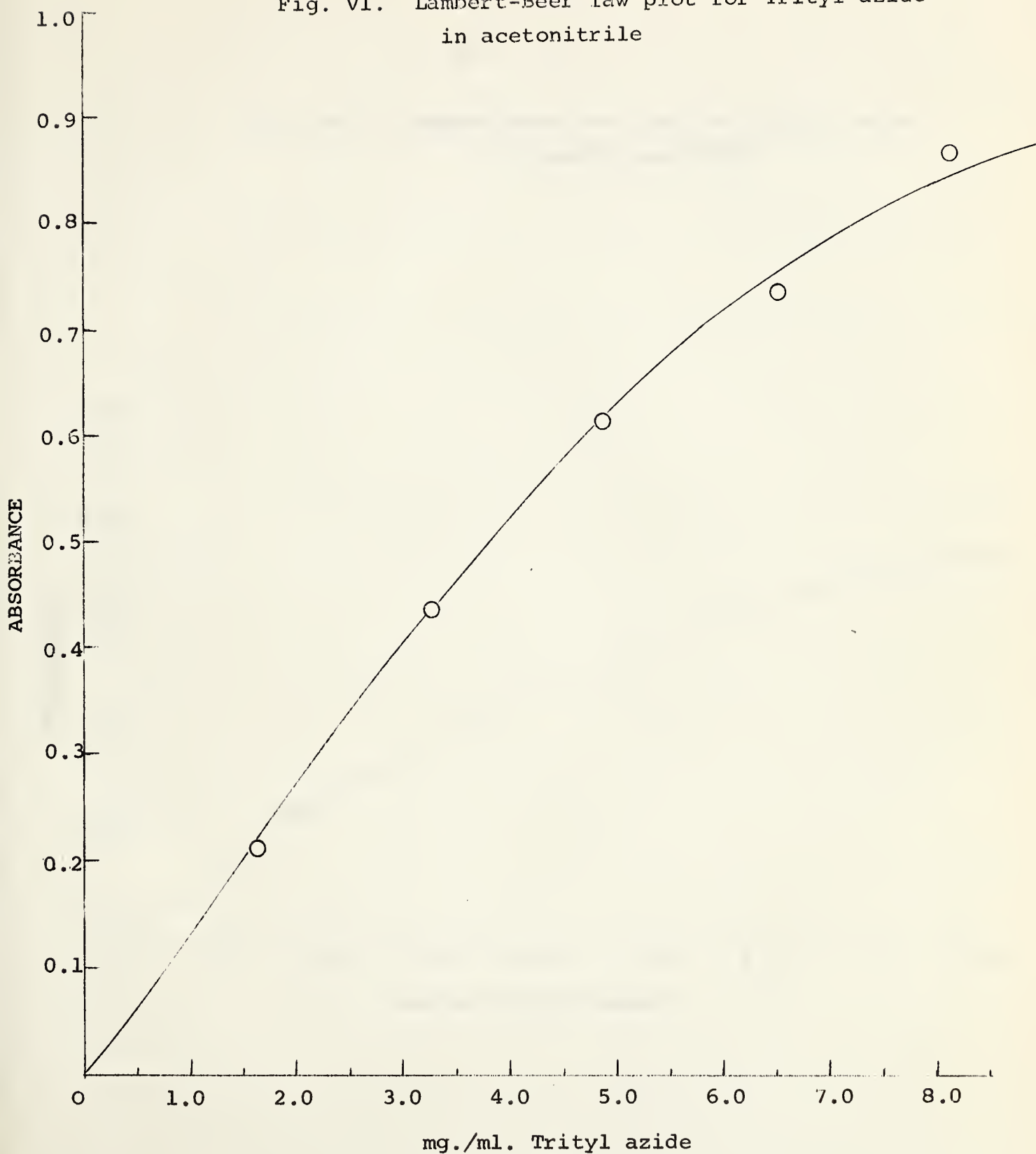
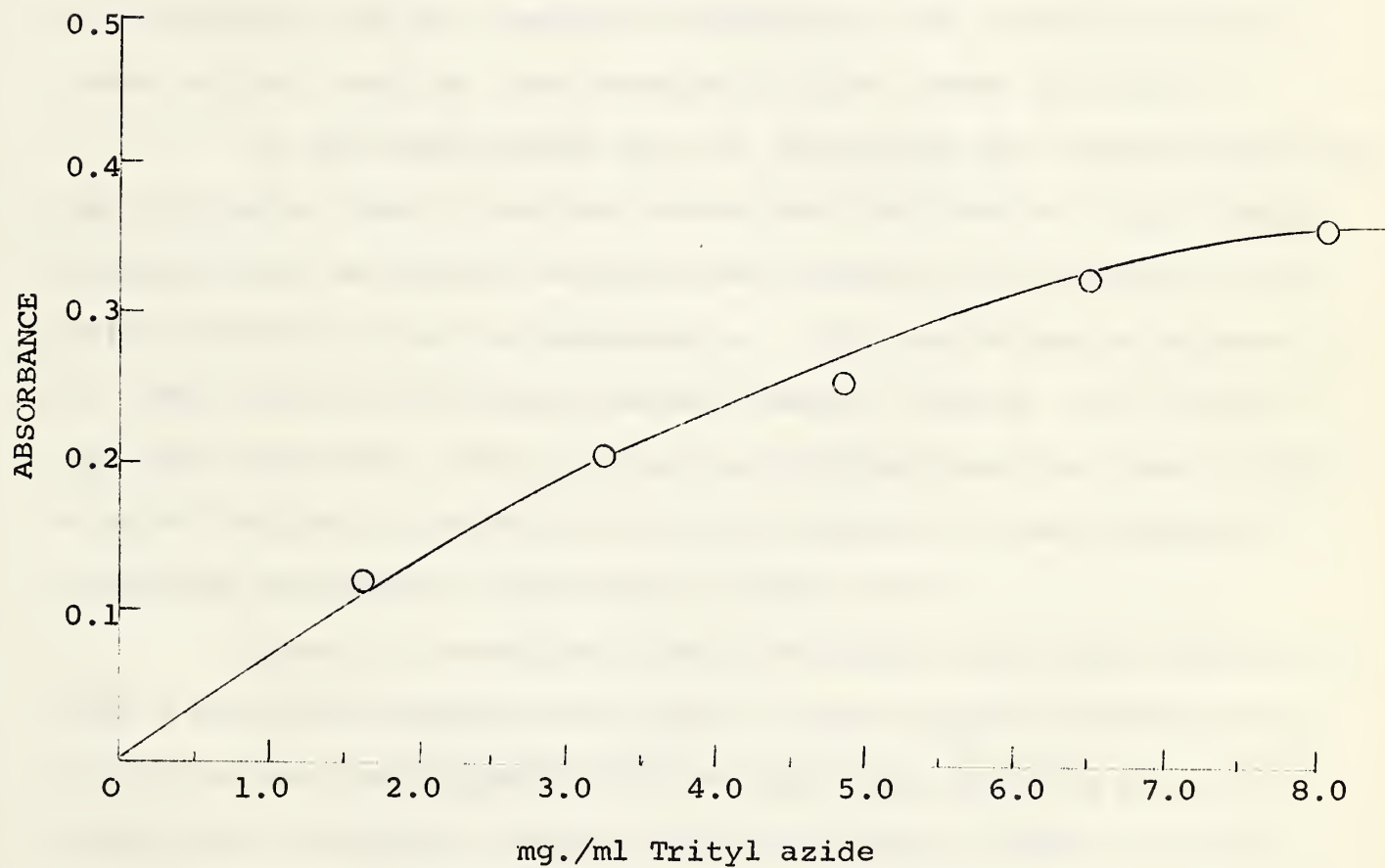


Fig. VII. Lambert-Beer law plot for Trityl azide
in dimethylsulfoxide



DISCUSSION

The relatively constant amount of trityl azide resulting in these substitution reactions, over a twentyfold change in concentration of the nucleophile, with a constant concentration of substrate, lends itself to the interpretation that a common trappable intermediate does not exist for all the sulfone and trityl azide in these solvents. This contrasts to the situation in chloroform discussed in Chapter II.

In interpretation, the lack of a common intermediate is consistent also with the observed first-order process, where the rate constant has not changed on increasing the concentration of ionic azide; that is, the reaction is first order in ester.

It was established that in chloroform the trappable species was ion pairs, and it was also shown that the rate of trityl azide formation was an overall second-order reaction, first-order in ion pairs and first-order in nucleophile. If this situation existed in these solvents, we should expect similar results, but this has not been observed. Thus, it must be invoked that the type of ionic species trapped by the nucleophile in acetonitrile and dimethylsulfoxide is different from that in chloroform.

There is insufficient data available from these results to make a decision regarding the types of ionic species present here. In chloroform the trappable species could have been ion pairs of either the intimate or solvent-separated type, or both. If the trappable species in chloroform was intimate ion pairs, then the trappable species in acetonitrile and dimethylsulfoxide must be either dissociated ions or solvent-separated ion pairs, or both species. If the intermediate trapped in chloroform was solvent-

separated ion pairs, or both intimate and solvent-separated ion pairs, then in the high dielectric solvents, the species trapped must be dissociated ions.

Previous data by Pocker (14) from studies of trityl chloride in nitromethane have shown dissociated ions to be the only ionic species present in this solvent. This might allow one to predict that the trappable species in this case to be dissociated ions, whence the rearrangement of the ester to sulfone would have occurred by way of ion pairs and not dissociated ions. The downward drift in rate observed at equimolar concentrations of 2-methyl ester and tetra-n-butylammonium azide in acetonitrile might be due to common ion rate depression, whence the aforementioned reasoning would be valid. Nevertheless, it should be reiterated that a delineation of the types of ionic species present is not possible, due to insufficient information at the present time.

The results in these solvents lend support to Mechanism II, the ionization mechanism, rather than to Mechanism I, the cyclic, non-ionizing mechanism. The increased observed rate of rearrangement in nitrobenzene, acetonitrile, dimethylsulfoxide and chloroform over carbon tetrachloride, is consistent with an ionization process, sensitive to solvents effects. The increased rate of exchange of trityl 2,6-dimethylbenzenesulfinatate with tetra-n-butylammonium azide in acetonitrile and dimethylsulfoxide, over chloroform, at the same concentrations of ester and ionic azide, is again consistent with an ionization process.

To the extent that the ionic azide captures the same percentage of carbonium ion for both the 2,6-dimethyl and 2-methyl esters, then the relative rates of exchange reflect the relative rates

of ionization for both esters. By a comparison of Run # 35 (Table XVI) with Run # 36 (Table XVI) it may be seen that the 2-methyl ester is approximately twelve times faster in exchange than the 2,6-dimethyl ester. This compares with a value of six to eight in chloroform. This factor of six to eight was determined by a comparison of the second-order rate constants for trityl azide formation for both compounds in chloroform in Runs (24 and 21) and (31 and 42).

EXPERIMENTAL

Reagents

Nitrobenzene was purified by use of a method suggested by Fieser (57) which involved steam distillation through an Eastman condenser, to which an Allihn condenser was attached. The distillate was dried by percolation through, and distillation from Linde 4-A molecular sieves; b.p. 90°C. at 14.8 mm. pressure; reported b.p. (57) 210°C at 760 mm.

Acetonitrile. - Fisher reagent grade acetonitrile was refluxed with, and distilled from phosphorus pentoxide. b.p. 80°C. at 7.0 mm. Hg.; reported b.p. 81.5 C. at 7.8 mm. Hg. (58).

Dimethylsulfoxide. - Using Baker and Adamson reagent grade solvent, purification was effected by use of a method suggested by Winstein (54). The solvent was dried three times by percolation through a 4 ft. column of Linde 4-A molecular sieves, from which it was distilled; b.p. 69°C. at 9 mm. Hg.; reported b.p. 69°C. at 9 mm. Hg. (54).

The preparation and purification of the other reagents used in this section have been previously described in Chapters I and II.

Procedures

N.M.R. Rate Determination for the Rearrangement of the 2-Methyl Ester in Nitrobenzene.

A 0.1215 M. solution of 2,6-lutidine in nitrobenzene was prepared by weighing 0.325 g. (0.0302 mole) of 2,6-lutidine into a tared 25 ml. volumetric flask to which nitrobenzene was then added to the mark. An aliquot of this solution was then added to 0.3970 g. (0.001 mole) of trityl 2-methylbenzenesulfinate in a 10 ml. volumetric flask until the mark was reached, giving a 0.10 M. solution of

sulfinate in nitrobenzene containing 0.1215 M. 2,6-lutidine. The concentrations used here were necessary for the detection of the methyl proton signals in the N.M.R.

On addition of the solvent to the ester the time was recorded. An aliquot of reaction mixture was then transferred to an N.M.R. sample tube to which a few drops of tetramethyl silane was added as an internal standard, and the region 5.0 to 10.0 τ was scanned using a Varian A-60 instrument. The region in which the singlets appear have already been summarized in Table XIV. The time recorded for a point in the run, was that at which the peak maximum was reached for the sulfone signal. After 46 min. the ester band had disappeared completely

Kinetic Procedure This has been previously described in Chapter II for the reactions in chloroform.

Reaction Products

Trityl 2-Methylphenyl Sulfone

After 10 half-lives, total spectra in acetonitrile revealed a doublet at 1125, 1145 cm.,⁻¹ which is characteristic for this compound, being absent from spectra of the other reaction products. No triphenylcarbinol was detected in these spectra.

The sulfone was isolated from dimethylsulfoxide in the following manner. Twenty-three ml. of the reaction mixture was added to a separatory funnel which contained 10 ml. of pyridine and 50 ml. of ether. Initially the reaction mixture contained 0.2603 g. ester and 0.6755 g. ionic azide per 25 ml. of solvent and is the same used for Run # 44. After washing the contents of the separatory funnel with three 50 ml. portions of water, the ether extract was dried over anhydrous magnesium sulfate and the solvent was removed

by evaporation under an aspirator tube to yield a pale yellow oil. Traces of pyridine were still detectable in the product, and were completely removed by further pumping under an oil pump vacuum for 30 min. in a pear-shaped flask which was warmed by a 70° C. water bath. A yield of 0.2206 g. of product was obtained. To the yellow oil was added 2 ml. of ether and 5 ml. of pentane to instantly yield a white precipitate which was filtered off from the solvent and washed with an additional 5 ml. of pentane. Infrared spectra in carbon disulfide showed the product to be mainly sulfone, with traces of trityl azide. An analysis of these spectra revealed at least 98.5% sulfone and 1.5% trityl azide to be present.

Pyridine was added (in this work-up procedure) in order to prevent any possible hydrolysis of the sulfone from occurring. Trityl azide was identified as a reaction product by its characteristic absorption at 4.79 microns in the infrared.

CHAPTER IV

The Reactions of some Tetra-n-butylammonium salts and 2,6-lutidine with Trityl perchlorate

These salt exchange experiments were conducted primarily with the intention of determining the types of reactions which the trityl cation would undergo with the arenesulfinate anions in the solvents used for the rearrangement and substitution studies of the esters. It was believed that the results from these studies would provide some information as to the reactions which could be ruled out in the rearrangements and substitution of the sulfonates.

RESULTS

Trityl perchlorate produces a brilliant yellow colour when dissolved in chloroform. The solubility of the salt is limited to ca. 4.4×10^{-3} mole/litre, and the characteristic Bactrian camel-shaped spectrum of the trityl cation, (with peaks at 405 and 425 millimicrons), was discernible in the ultraviolet.

The yellow colour of the chloroform solution was instantly discharged on addition of an equimolar amount of tetra-n-butylammonium azide at room temperature, and trityl azide was found to be quantitatively produced in the reaction. This was observed from infrared spectra taken 15 minutes after mixing. A spectrum of the same solution taken 63 minutes after mixing the reactants, showed no further change in the trityl azide band. Added 2,6-lutidine did not affect the yields of trityl azide. The data are presented in Table XVIII.

The yellow colour was not discharged when tetra-n-butylammonium perchlorate was added to the salt solution.

The reaction of tetra-n-butylammonium 2-methylbenzene-

Table XVIII.

The substitution of trityl perchlorate with various tetra-n-butylammonium salts in chloroform

at 25°C.^a

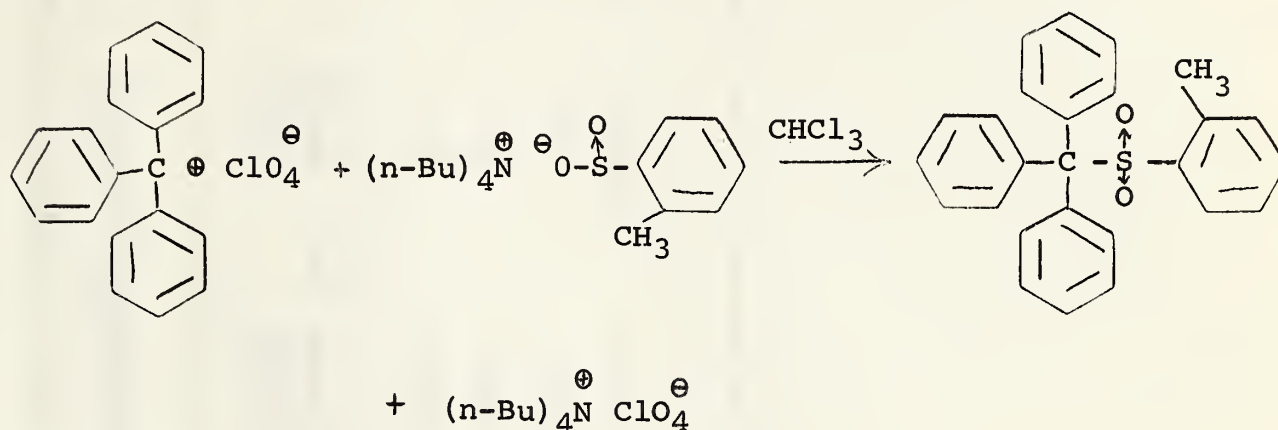
Experiment	Trityl perchlorate (M.)	2,6-lutidine (M.)	(n-Bu) ₄ N [⊕] salt	(M.)	Reaction time ^b (min.)	Product ^c
26	0.0388	-	azide	0.0384	15	Trityl azide
27	0.0480	0.0448	azide	0.0480	63	"
28	0.0350	0.0448	2-methyl sulfinate	0.0350	9	"
					10	2-methyl sulfone
					149	"
30	0.0332	-	2,6-dimethyl sulfinate	0.0296	16	2,6-dimethyl ester

^a The colour change involved for each reaction is yellow to colourless.

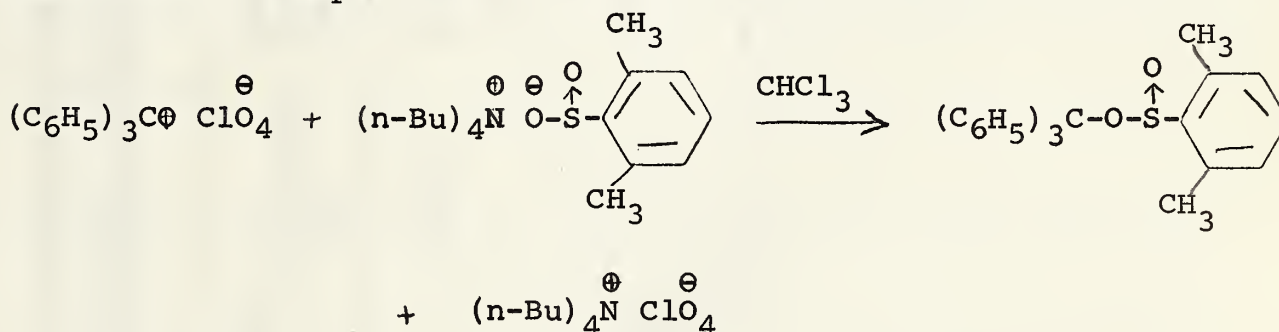
^b Represents the time interval between mixing reactants and running spectrum.

^c Obtained in quantitative yields.

sulfinate and trityl perchlorate in chloroform, with added 2,6-lutidine, quantitatively produced trityl 2-methylphenyl sulfone. From spectra taken 24 and 149 minutes after mixing the reactants, the sulfone band showed no change relative to spectra taken 10 minutes after mixing.



Tetra-*n*-butylammonium 2,6-dimethylbenzenesulfinate under similar reaction conditions, exchanged to produce trityl 2,6-dimethylbenzenesulfinate as the product. No sulfone resulted from the reaction.



No triphenylcarbinol was found as a product from either of these two exchange processes. These data are summarized in Table XVIII.

Competition experiments between azide ion and the 2-methylbenzenesulfinate anion for the trityl cation, in chloroform, have shown the azide ion to be two to three times more effective as a nucleophile than the sulfinate anion. A product ratio of 2-3:1 for trityl azide and 2-methylphenyl sulfone always resulted, whether

Table XIX.

The substitution of trityl perchlorate with mixtures of tetra-n-butylammonium azide and 2-methylbenzenesulfinate in chloroform and acetonitrile at 25°C.

Experiment	Trityl perchlorate (M.)	Solvent	2,6-lutidine (M.)	(n-Bu) ₄ N [⊕] azide (M.)	(n-Bu) ₄ N [⊕] 2-methyl sulfinate (M.)	% Trityl azide	% 2-methyl sulfone
29	0.0252	Chloroform	0.0448	0.0705	0.0705	67.5	32.5
34-B	0.0252	"	-	0.0695	0.0695	65.0	35.0
53	0.0264	"	-	0.0743	0.0745	70.0	30.0
55	0.0267	Acetonitrile	-	0.0712	0.0710	ca.69.6	ca.30.4

the exchanges were conducted in the presence, or absence, of 2,6-lutidine (see Table XIX).

The triphenylmethyl cation was found to undergo reaction with 2,6-lutidine in chloroform, and in acetonitrile. The extinction coefficient of the trityl cation in chloroform has a value of 1.739×10^4 , and knowing this value, the concentration of the carbonium ion could be determined in mixtures of trityl perchlorate and 2,6-lutidine. When a 2:1 mole ratio of trityl perchlorate to 2,6-lutidine was maintained, the yellow colour was not completely discharged, and the concentration of the trityl cation was found to be reduced by one half of its original absorbance value in the absence of 2,6-lutidine. This indicates that one mole of 2,6-lutidine has reacted with one mole of trityl perchlorate. When a mole ratio of 126:1 for 2,6-lutidine and trityl perchlorate was maintained, the yellow colour was discharged completely, and the colourless solution showed no absorption for the trityl cation. These data are presented in Table XX.

Table XX.

Compound formation of trityl perchlorate with 2,6-lutidine in chloroform at 25°C.

Trityl perchlorate (M. $\times 10^5$)	2,6-Lutidine (M. $\times 10^5$)	Trityl cation absorbance
4.439	-	0.772
4.439	556	-
8.878	4.037	0.760

When perchloric acid was added to the colourless chloroform solution resulting from the reaction of the two compounds, the yellow colour was regenerated, gradually intensifying over a period of an

hour. The mixture was vigorously stirred to allow interaction of the two-phase system.

Qualitative experiments conducted with trityl perchlorate and pyridine in chloroform, gave the same discharge of the yellow colour which was observed for 2,6-lutidine. However, with benzene, no reaction was detectable, and the yellow colour was maintained. When solutions of trityl perchlorate in chloroform were swamped with 2,6-lutidine, in addition to the immediate decolourization observed, the solution changed from colourless to green, and then to purple. Discharge of the purple colour occurred after sitting at room temperature for four hours. This could probably be due to some type of oxidation - reduction reaction.

An attempted determination of the extinction coefficient for the trityl cation in acetonitrile was unsuccessful, since reproducible results could not be obtained, and the values were observed to change with time. This could possibly have resulted from reaction of the carbonium ion with the solvent or with trace impurities. An example of the type of results obtained is given in Table XXI, and plots of concentration versus absorbance to show the irreproducibility of the method, is given in Fig. VIII.

In dimethylsulfoxide, compound formation results from a reaction of trityl perchlorate and the solvent. The characteristic Bactrian camel-shaped spectrum for the trityl cation was not discernible in the ultraviolet, and the intensity of the yellow colour was considerably reduced, even at high salt concentrations. Spectra showed a maximum between 270 and 290 millimicrons. These data are given in Table XXII. Attempts to trap the carbonium ion were successful only when the nucleophile was added to the solvent

Table XXI.

The change of absorbance with time for trityl perchlorate in
acetonitrile at 25°C.

Trityl perchlorate 1.593×10^{-4} M.

<u>Wavelength</u> (millimicrons)	<u>Absorbance</u>	<u>Time</u> (minutes)
405	1.87	21
	1.85	41
	1.90	73
	1.89	107
	1.89	141
	1.86	200
	1.67	420
	1.19	886
420	1.80	23
	1.80	42
	1.85	75
	1.81	109
	1.79	145
	1.76	202
	1.58	422
	1.13	888

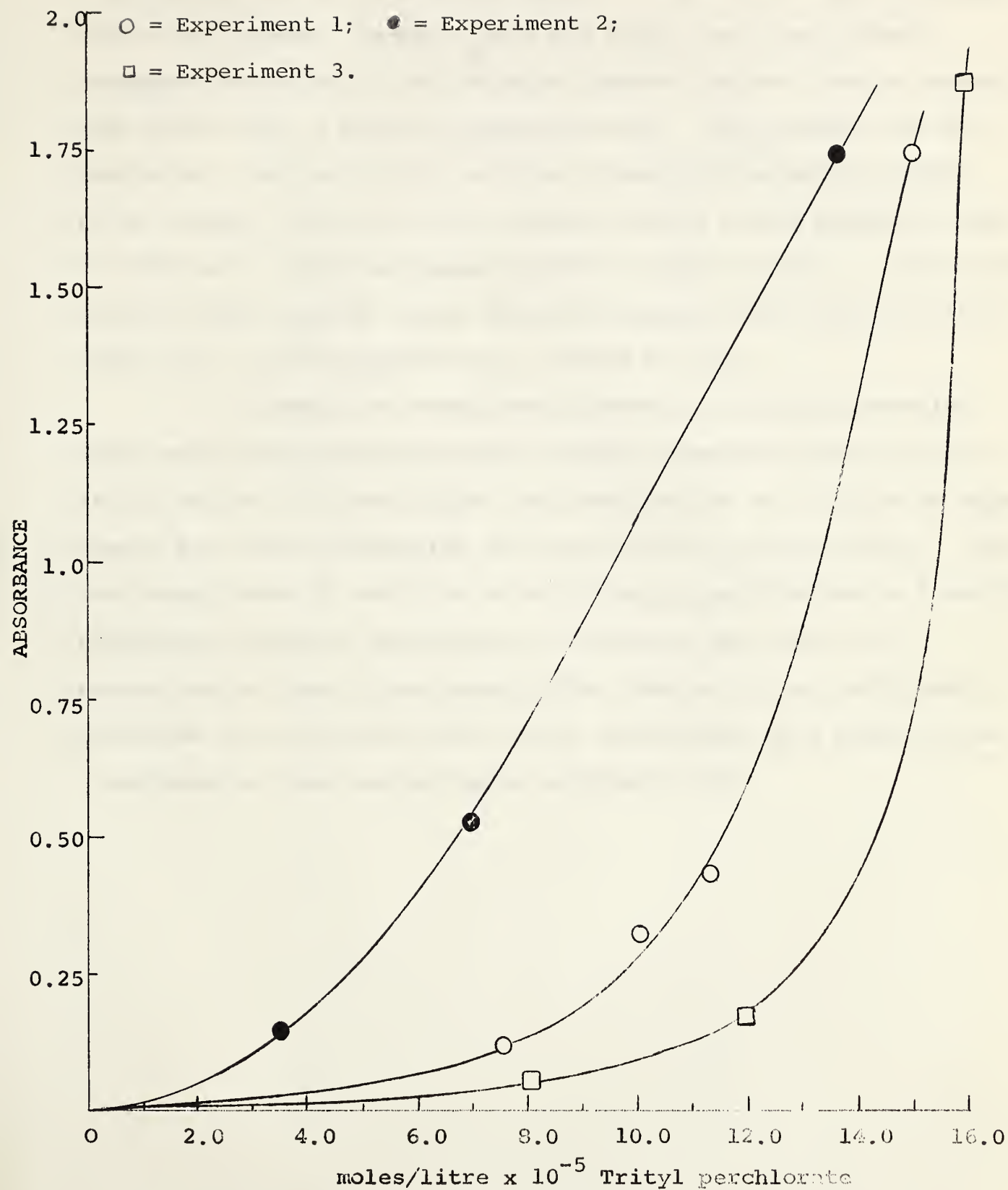


Fig. VIII Lambert-Beer law plots for Trityl perchlorate in acetonitrile to show irreproducibility of determinations.

before addition of trityl perchlorate. If the perchlorate was present in the solvent before adding the azide ion, only 15% trityl azide was isolated, compared with 91% using the other method. Attempted isolation of the reaction product yielded a white crystalline solid after a work-up involving water. The product was not identified, but its N.M.R. spectrum showed only aromatic protons to be present, while its I.R. spectrum showed a very prominent band at 1060 cm.^{-1} , which is characteristic of alkyl ethers. The isolated product after work-up, could therefore possibly have been ditrityl ether m.p. = 150°C (reported m.p. $237-238^{\circ}\text{C}$ (59)).

A competition experiment between tetra-n-butylammonium azide and tetra-n-butylammonium 2-methyl benzenesulfinate for the trityl cation in acetonitrile, was conducted so as to allow an equal chance for both nucleophiles to react with the trityl cation. This was accomplished by addition of solid trityl perchlorate to a solution containing equimolar quantities of sulfinate and azide at a concentration three times greater than that of trityl perchlorate. The azide ion was found to be two to three times more effective as a nucleophile than the sulfinate ion (Table XIX).

Table XXII.

Absorbance values in the ultraviolet for compound formation
between the trityl cation and dimethylsulfoxide

Trityl perchlorate = 3.873×10^{-2} M.

<u>Wavelength</u> (millimicrons)	<u>Absorbance</u>
267	3.0
270	∞
275	∞
280	∞
330	0.800
335	0.765
340	0.735
350	0.675
360	0.650
370	0.635
380	0.615
390	0.569
400	0.502
410	0.430
420	0.369
440	0.268
450	0.230
460	0.184
470	0.105
480	0.080
490	0.072

DISCUSSION

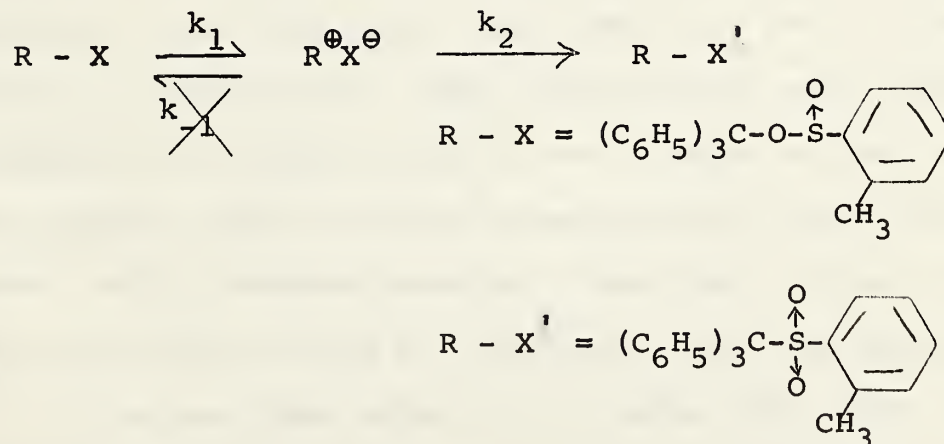
From these data some information on the reactions of the trityl cation with the 2-methylbenzenesulfinate and 2,6-dimethylbenzenesulfinate anions, as well as with 2,6-lutidine, has been made available.

The base 2,6-lutidine was used in conjunction with the salts in these experiments in an attempt to duplicate the reaction conditions used in the rearrangement and substitution reactions, and also to prevent any possible acid catalysis which might occur. From the data presented in Table XX, it has been shown that 2,6-lutidine undergoes a reaction with the trityl cation, an observation which differs from the conclusions of other workers with similar systems (15, 39, 40, 42). The question arises as to the reactive site where tritylation occurred in the 2,6-lutidine molecule. One might have reasoned that the steric bulk associated with the trityl cation, and that associated with the methyl groups in the 2- and 6- positions of the lutidine molecule, would eliminate the possibility of reaction occurring at nitrogen. On this basis, a more feasible prediction would be that reaction occurred at the ring in a manner analogous to the Friedel-Crafts reaction. However, benzene was found to undergo no reaction with the trityl cation, thus ruling out a Friedel-Crafts type reaction. We therefore conclude that tritylation of 2,6-lutidine occurred at nitrogen. Whether covalent bond formation occurs with localization of charge, or whether a π complex is produced is unknown.

The reasons for using 2,6-lutidine as a base in the reactions of the arenesulfates were previously outlined in Chapter I. In these reactions 2,6-lutidine, in addition to neutralizing trace

quantities of acid which might be present, could also act as a competing nucleophile along with the arenesulfinate and azide anions. However, these competition salt exchanges have shown this base to have no effect on the substitution or rearrangement processes since trityl azide and trityl 2-methylphenyl sulfone product distribution was unaffected in its presence or absence.

The reaction of trityl perchlorate with tetra-*n*-butylammonium 2-methylbenzenesulfinate to give only trityl 2-methylphenyl sulfone and no ester, was shown by the fact that no change in the sulfone band occurred 149 minutes after mixing, compared to 24 minutes after mixing (Table XVIII). If ester had been produced by attack of the sulfinate oxygen on the carbonium ion, then over this period of time it would have rearranged to give sulfone, and an increase in sulfone absorbance would have been detected. Interpretation of these observations leads to the conclusion that ion pair return to give starting ester is negligible in the trityl 2-methylbenzenesulfinate system. Once the ion pair is generated, sulfone, and no ester, is produced, or k_2 is much greater than k_{-1} :



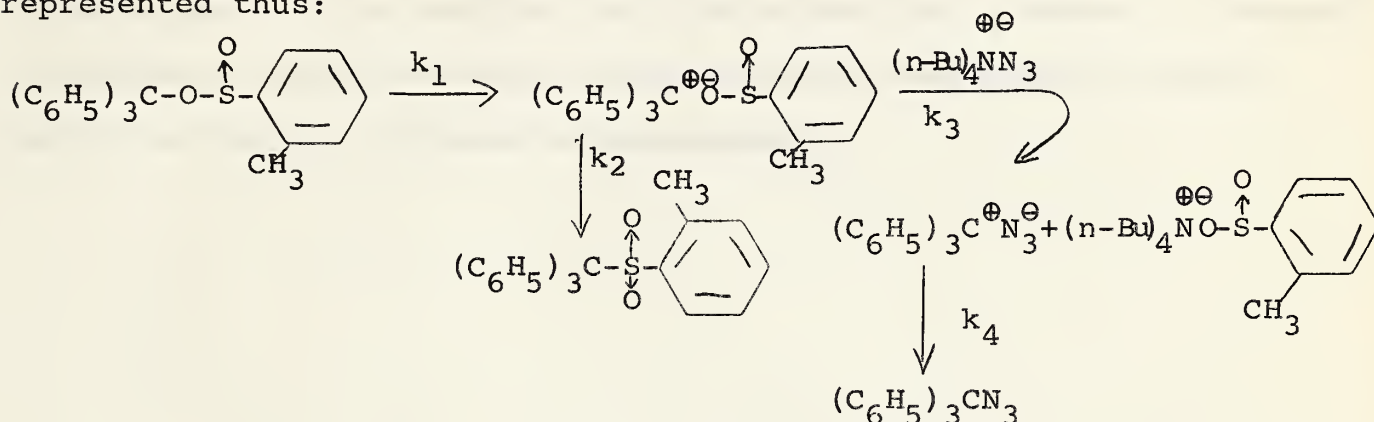
The very rapid reactions of these salts to give sulfone, suggest that the energy barrier to sulfone formation from the intermediate ion pair, must be considerably lower than that for the generation of the ion pair from starting ester. In other words, the slow and rate-determining step in the rearrangement is the ionization step.

In the reaction of tetra-n-butylammonium 2,6-dimethylbenzenesulfinate with trityl perchlorate in chloroform, no sulfone was produced, but only starting ester was recovered (Table XVIII). This is consistent with the results described in Chapter I, where attempts to synthesize trityl 2,6-dimethylphenyl sulfone proved to be unsuccessful. Apparently, a high energy barrier exists to sulfone formation due to steric hindrance. This means that there are lower energy barriers to carbon-oxygen than to sulfur-oxygen bond formation here, and ion pair return to regenerate starting ester becomes highly significant, or $k_{-1} > k_2$ for this system.

Competition experiments between azide ion and 2-methylbenzenesulfinate anion for the trityl cation in chloroform and acetonitrile, have shown the azide ion to be two to three times more effective as a nucleophile than the sulfinate anion (Table XIX). No comparative nucleophilicity of two or more anionic species for an electrophile using salts as substrates has been previously recorded, and it becomes important here that a direct comparison between the azide ion and the sulfinate anion has been made available.

The fact that azide ion is three times more effective as a nucleophile than the sulfinate anion in the salt exchanges, indicates that for the ester systems, ion pair collapse to produce sulfone must be faster than exchange with azide ion since only 2%

azide was produced at equimolar quantities of both. If this were not so, then on the basis of the relative nucleophilicities of the azide and sulfinate anions, at least 60 to 70% capture of the carbonium ion would have occurred at equimolar concentrations. This may be represented thus:



In other words, if the reverse rates are negligible compared to the forward rates, then on the basis of the reasoning proposed above, k_2 should be at least 2 to 3 or more than 3 times greater than $k_3[N_3^-]$.

Competition experiments in acetonitrile revealed a 2:1 product ratio for trityl azide and sulfone. In the 2-methyl ester systems, the maximum percentage of trityl azide produced in the concurrent rearrangement and substitution was 42%, and an average value of 36% trityl azide resulted on varying the concentration of ionic azide from 0.02 to 0.05 M at a constant ester concentration (0.02 M.) The fact that a 2:1 product ratio for trityl azide and sulfone resulted in the salt exchange competition experiments would tend to suggest that at least 60-70% trityl azide should be produced at equimolar concentrations of ester and ionic azide. A value of 36% was obtained, suggesting again that ion pair collapse to give sulfone must be faster than exchange to give trityl azide. Furthermore,

in chloroform at equimolar concentrations of ester and ionic azide, only 2% trityl azide resulted compared with 36% in acetonitrile. If a similar situation existed in both solvents then one would expect a similar amount of trapping to occur. These data therefore lend support to the previous interpretations that a common, capturable intermediate does not exist for the greater percentage of trityl azide and sulfone produced in acetonitrile.

EXPERIMENTAL

Reagents

Trityl perchlorate. - The salt was prepared by use of a recent procedure suggested by Dauben (60). Starting with 0.0385 mole (10 g.) triphenylcarbinol, and 12.5 ml. of 70% perchloric acid, 11 g. of crude product was obtained; yield = 84.5%. On recrystallization from hot, dry acetonitrile, a 31% recovery was effected; m.p. 144-145°C, reported m.p. 143°C. The precautions suggested by Dauben in the storage and use of the salt were exercised.

Procedures

Reactions of trityl perchlorate and tetra-n-butylammonium salts

The quarternary ammonium salt was weighed out in a tared volumetric flask, and a few ml. of solvent was added, and the volume made up to the mark with solvent. After dissolution of the perchlorate the spectra were taken on a PE 21 instrument, by scanning over the appropriate range.

Competition Experiments between azide ion and sulfinate ion for trityl perchlorate

In order to allow for an equal chance of attack on the carbonium ion by the respective nucleophiles, equal concentrations of both salts were used, the concentrations being three times greater than trityl perchlorate. A typical procedure will be given here using Run 29 as an example.

Tetra-n-butylammonium azide (0.2008 g.; 0.000705 mole) was weighed into a tared 50 ml. erlenmeyer flask. Tetra-n-butylammonium 2-methylbenzenesulfinate (0.2797 g.; 0.000705 mole) was separately weighed on a watchglass, and then added to the solid azide. Both salts were then brought into solution by the addition of 5 ml. of a 0.0448 M. solution of 2,6-lutidine in chloroform to the solid salt

mixture using an automatic 5 ml. pipette. To this solution was added 0.0864 g. (0.000252 mole) of trityl perchlorate, and the solution was vigorously stirred to assist in the dissolution of the salt. An additional 5 ml. of solvent was then added to give the required concentrations.

A sample of the solution was then transferred to a 0.5 mm. matched cell, and the sulfone and trityl azide regions (7.3 to 8.1 and 4.6 to 5.3 microns respectively) were scanned on a PE 21 instrument. The absorbance value for trityl azide was found to be 0.3980, corresponding to 2.91 mg./ml. or 0.0102 M. in trityl azide. The optical density of the sulfone produced was 0.0551 or 1.95 mg./ml., corresponding to a 0.00491 M. solution. Thus, 67.5 mole% trityl azide, and 32.5 mole % sulfone were produced as reaction products.

Determination of the extinction coefficient of trityl perchlorate in chloroform

Trityl perchlorate (0.0866 g.; 0.000252 mole) was added to 25 ml. of chloroform in a tared erlenmeyer flask and the mixture allowed to sit at room temperature for 1 hr., after which time, the undissolved salt was filtered off using a tared sintered-glass funnel under the house-vac. The weight of undissolved salt in the funnel and the erlenmeyer flask was found to be 0.0486 g.; indicating that 0.0380 g. (0.000111 mole) of perchlorate had dissolved in 25 ml. of chloroform to yield a 4.439×10^{-3} M. solution. One ml. of this solution was then transferred to a 100 ml. volumetric flask, and solvent added to bring the volume up to the mark to give a 4.439×10^{-5} M. solution. The absorbance of this solution was measured by scanning the range 300 to 600 millimicrons on a Cary recording visible-ultra-violet spectrophotometer in 1 cm. matched cells. The absorbance

of the trityl cation was found to be 0.772 at 415 millimicrons. At 405 and 425 millimicrons, the absorbance values were found to be 0.784 and 0.760 respectively. The calculated extinction coefficient of 1.739×10^4 was based on the optical density of 0.772 at 415 millimicrons.

The reaction of 2,6-lutidine with trityl perchlorate

The procedure for a typical experiment will be described.

The 4.439×10^{-3} M. solution of trityl perchlorate in chloroform prepared for use in the determination of the extinction coefficient was the same solution used in these experiments.

Using an automatic 1 ml. pipette, 1 ml. of this 4.439×10^{-3} M. solution was transferred to a 100 ml. volumetric flask to which 1 ml. of 4.037×10^{-3} M. 2,6-lutidine in chloroform was added, and the volume made up to the mark by addition of chloroform. This gives a solution which is 8.878×10^{-5} M. in trityl perchlorate and 4.037×10^{-5} M. in 2,6-lutidine. At this stage the yellow colour of the solution was still discernible. The absorbance of the solution was measured as previously described for the determination of the extinction coefficient, and the absorbance at 415 millimicrons was found to be 0.76, (0.78 at 405 and 0.74 at 425 millimicrons) which corresponds to a concentration of 4.371×10^{-5} M. in trityl cation. This compares with a starting concentration of 8.878×10^{-5} M.

Attempted determination of the extinction coefficient of the trityl cation in acetonitrile

A typical example of these experiments will be given here.

A 3.394×10^{-2} M. solution of trityl perchlorate in acetonitrile was prepared by adding 0.2725 g. (0.000795 mole) of trityl perchlorate (93.8% pure) to a 25 ml. volumetric flask to which solvent

was added to the mark. Using an automatic 5 ml. pipette, 5 ml. of this solution was transferred to a 25 ml. volumetric flask and solvent added to the mark to give a 6.788×10^{-3} M. solution. Solutions of concentrations 1.3576×10^{-4} M., 0.6878×10^{-3} M. and 0.3394×10^{-4} M. were prepared by dilution of 1 ml. samples of this standard solution to 50, 100 and 200 ml. respectively, using the appropriate size volumetric flask and the same 1 ml. automatic pipette.

The range 330 to 450 millimicrons was scanned for one of these samples in matched 1 cm. Beckman cells thermostated at 25.4°C., and using a Beckman DU spectrophotometer. The characteristic spectrum for the trityl cation with peaks at 405 and 425 millimicrons was discernible. After this, the absorbances of the samples were determined at 405 and 420 millimicrons.

The reaction of trityl perchlorate with dimethylsulfoxide

A 0.028 M. solution of trityl perchlorate was prepared by dissolving 0.334 g. (0.00098 mole) of salt in 5 ml. of dimethylsulfoxide, in a 25 ml. volumetric flask which was then made up to the mark with solvent to give a pale yellow solution. Absorbance measurements on a Beckman DU instrument (in 1 cm. cells thermostated at 25.4°C.) over the range 267 to 490 millimicrons (Table XXII), revealed a maximum at 270 to 280 millimicrons with a tail stretching into the visible region.

One hour after preparing the solution of salt in dimethylsulfoxide, 5 ml. of this solution was added to an erlenmeyer flask containing 0.0270 g. (0.0000955 mole) of tetra-n-butylammonium azide and 0.0508 g. (0.000475 mole) of 2,6-lutidine. A sample of this solution was scanned in the region 4.6 to 5.2 microns in the infrared using a PE 21 instrument and 0.5 mm. matched cells. The peak for

the trityl azide band was found to have shifted from 4.79 to 4.76 microns, and the observed absorbance of 0.5276 corresponded to a concentration of 0.0141 M. in trityl azide.

The solution was worked-up by adding 5 ml. of the reaction mixture to 30 ml. of ether, followed by two washings with 50 ml. portions of water. The ether extract was dried over anhydrous magnesium sulfate and the solvent removed by evaporation under an aspirator. To the white solid isolated, 5 ml. of chloroform was added, and an infrared spectrum of this solution revealed the concentration of trityl azide isolated to be 4.21×10^{-3} M. which corresponds to a 15.05% yield, based on the starting concentration of trityl perchlorate.

This experiment was repeated at the same concentrations, but the order of addition of the reactants was reversed, that is, tetra-n-butylammonium azide was first added to the dimethylsulfoxide, followed by addition of trityl perchlorate to this solution. On isolation of the product, infrared spectra revealed that 90.7% trityl azide was produced as reaction product. When trityl azide alone was carried through the work-up procedure, 98% recovery was effected.

Competition Experiment between azide ion and sulfinat ion for trityl perchlorate in acetonitrile.

In experiment 55 tetra-n-butylammonium azide (0.2019 g.; 0.000712 mole) was weighed into a tared 50 ml. erlenmeyer flask. Tetra-n-butylammonium 2-methylbenzenesulfinate (0.2816 g.; 0.000710 mole) was separately weighed on a watchglass, and then added to the solid azide. Both salts were then brought into solution by the addition of 5 ml. of acetonitrile to the solid salt mixture

using an automatic 5 ml. pipette. To this solution was added 0.0914 g. (0.000267 mole) of trityl perchlorate, and the solution was vigorously swirled to assist in the dissolution of the salt. An additional 5 ml. of acetonitrile was then added to give the required concentrations.

Twenty minutes after mixing, a sample of the solution was then transferred to a 0.5 mm. matched cell and the trityl azide region (4.6 to 5.3 microns) was scanned on a PE 21 instrument. The sulfone band could not be scanned here since acetonitrile absorbs in the region of 7.3 to 8.1 microns. The absorbance value for trityl azide was found to be 0.5661, corresponding to 4.35 mg./ml. or 0.0153 M. The trityl perchlorate used in this run was 82.5% pure, this value being obtained from the results of experiment 53 in chloroform. The percentage of trityl azide produced here was based on 82.5% pure trityl perchlorate and the percentage of sulfone obtained by difference since trityl azide was the only other reaction product. On this basis, 69.6% trityl azide and 30.4% sulfone resulted from this experiment.

Reaction Products

The methods of identification of the reaction products have been previously described in Chapters II and III.

BIBLIOGRAPHY

1. P. Walden, Ber., 35, 2018 (1902).
2. M. Gomberg, *ibid.*, 35, 2403 (1902).
3. K. Ziegler and H. Wollschitt, Ann., 479, 90 (1930).
4. K. Ziegler and W. Mathes, *ibid.*, 479, 111 (1930).
5. S.T. Bowden and T.L. Thomas, J. Chem. Soc., 1242 (1940).
6. N. Lichtin and P.D. Bartlett, J. Am. Chem. Soc., 73, 5530 (1951).
7. N. Lichtin and P.D. Bartlett, *ibid.*, 73, 5537 (1951).
8. K. Ziegler and H. Wollschitt, Ann., 479, 108 (1930).
9. J.E. Leffler, "The Reactive Intermediates of Organic Chemistry", Interscience Publishers, Inc., New York, (1956), p. 82.
10. A. Bentley, A.G. Evans and J. Halpern, Trans. Farad. Soc., 47, 711 (1951).
11. B.B. Smith and J.E. Leffler, J. Am. Chem. Soc., 77, 1700 (1955).
12. J.W. Bayles, A.G. Evans and J.R. Jones, J. Chem. Soc., 1020 (1957).
13. W.B. Smith and P.S. Rao, J. Org. Chem., 26, 254 (1961).
14. Y. Pocker, J. Chem. Soc., 240 (1958).
15. C.G. Swain, J. Am. Chem. Soc., 70, 1119 (1948).
16. C.G. Swain, *ibid.*, 72, 2794 (1950).
17. C.G. Swain, C.B. Scott and K.H. Lohmann, *ibid.*, 75, 136 (1953).
18. C.G. Swain and M.M. Kreevoy, *ibid.*, 77, 1122 (1955).
19. C.G. Swain and R.B. Mosely, *ibid.*, 77, 3727 (1955).
20. C.G. Swain, R.B. Mosely, and D.E. Brown, *ibid.*, 77, 3731 (1955).
21. C.G. Swain, L.E. Kaiser and T.E. Knee, *ibid.*, 77, 4681 (1955).
22. C.G. Swain and E.E. Pegues, *ibid.*, 80, 812 (1958).
23. C.G. Swain and A. MacLachlan, *ibid.*, 82, 6095 (1960).
24. M.F. Hawthorne and D.J. Cram, *ibid.*, 76, 3451 (1954).
25. C.K. Ingold and co-workers, J. Chem. Soc., 1206-1265 (1957).

26. R.F. Hudson and B. Saville, J. Chem. Soc., 4130 (1955).
27. S. Winstein, P.E. Klinedinst, Jr., and G.C. Robinson, J. Am. Chem. Soc., 83, 885 (1961).
28. C.L. Arcus, M.P. Balfe and J. Kenyon, J. Chem. Soc., 485 (1938).
29. A.C. Cope, D.E. Morrison and L. Field, J. Am. Chem. Soc., 72, 59 (1950).
30. A.H. Wragg, J.S. McFayden and T.S. Stevens, J. Chem. Soc., 3603 (1958).
31. C.A. Bunton and B.N. Hendy, J. Chem. Soc., 2562 (1962).
32. C.A. Bunton and B.N. Hendy, *ibid.*, 627 (1963).
33. H.F. Herbrandson and C.M. Cusano, J. Am. Chem. Soc., 83, 2124 (1961).
34. D. Darwish and R. McLaren, Tetrahedron Letters, 26, 1231 (1962).
35. A.I. Vogel, "A Text-Book of Practical Organic Chemistry", Third Edition Longmans Green and Co., (1955), p. 501.
36. H. Phillips, J. Chem. Soc., 2575 (1925).
37. H.C. Brown and C.P. Garg, J. Am. Chem. Soc., 83, 2952 (1961).
38. H. Bohme and H. Fischer, Ber., 75 B, 1310 (1942); Chem. Abstr. 37, 4686 (1943).
39. E.S. Gould, "Mechanism and Structure in Organic Chemistry", Henry Holt and Co., New York, (1960), p. 277.
40. R.A. Benkeser, R.F. Grossman and F.S. Clark, J. Org. Chem., 27, 3728 (1962).
41. D.V. Hardy, J. Chem. Soc., 1000 (1929).
42. R.A. Benkeser and F.S. Clark, J. Org. Chem., 27, 3727 (1962).
43. J.F. Norris and R.C. Young, J. Am. Chem. Soc., 46, 2580 (1924).
44. O. Hinsberg, Ber., 50, 468 (1917).
45. D.C. Gregg, K. Hazelton and T.F. McLeon, J. Org. Chem., 18, 36 (1953).
46. C. Djerassi and R.R. Engle, J. Am. Chem. Soc., 75, 3838 (1953).

47. L.F. Fieser, "Experiments in Organic Chemistry", Third Edition, D. Heath and Co., Boston, (1957), p. 286.
48. L.F. Fieser, *ibid*, p. 284.
49. M.E. Hanke, J. Am. Chem. Soc., 45, 1321 (1923).
50. L.J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley and Sons, Inc., New York, (1958), p. 362.
51. C. Finzi and V. Bellavita, Gazz. Chim. Ital., 62, 699 (1932); Chem. Abstr. 27, 91 (1933).
52. A.I. Vogel, "A Text-Book of Practical Organic Chemistry", Third Edition, Longmans Green and Co., (1955), p. 826.
53. L.F. Fieser, "Experiments in Organic Chemistry", Third Edition, D. Heath and Co., Boston, (1957), p. 77.
54. S.G. Smith, A.H. Fainberg and S. Winstein, J. Am. Chem. Soc., 83, 625 (1961).
55. D. Darwish, U.C.L.A. Thesis (1958).
56. A. Illiceto, A. Fava and V. Mazzuccato, J. Org. Chem., 25, 1445 (1960).
57. L.F. Fieser, "Experiments in Organic Chemistry", Third Edition, D. Heath and Co., Boston (1957), p. 290.
58. L.F. Fieser, *ibid.*, p. 282.
59. J.O. Halford, J. Am. Chem. Soc., 51, 2157 (1929).
60. H.J. Dauben, Jr., L.R. Honnen and K.M. Harmon, J. Org. Chem., 25, 1442 (1960).

